ANILINE AS SOLVENT FOR THE SEPARATION OF AROMATIC COMPOUND FROM PARAFFIN BY LIQUID-LIQUID EXTRACTION

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INTRODUCTION

Fractional distillation has long been employed by refineries for refining of petroleum products. In certain instances, however, this technique is found inconvenient. For example, in the case of some systems, substantially complete separation by simple fractional distillation is impossible because of the formation of an azeotrope. In other instances, it is found that the operation is not economical because of the requirement of a large amount of heat and cooling water for reflux, and large equipment. In recent years, liquid extraction has rapidly assumed major industrial significance as a means of separating the components of solutions. It is now fully recognized that liquid-liquid extraction can be successfully used for enrichment or partial separation of fractions comprised of hydrocarbons of different structures.

It is known that certain aromatic components in crude petroleum have considerably higher antiknock value than the paraffinic components. It is of interest to know whether it is possible to apply the method of liquid-liquid extraction in the refining of petroleum so as to obtain fractions richer in aromatic compounds, and hence increasing its value as motor fuel and aviation fuel. It is also desirable to know whether the process, if applicable, is more economical than fractional distillation. Before such questions can be answered, considerable data of a physical-chemical nature must be obtained. These data form the fundamentals upon which the development of the liquid-liquid extraction process may be based. Among these data are the solubility relation, mutual solubility and distribution coefficients for the constituents

involved. A knowledge of the phase equilibrium relation of the constituents involved allows the prediction of the applicability of the process and permits a mathematical treatment of the extraction methods that may be used. However, these data cannot yet be predicted accurately, but must be obtained experimentally. It is the purpose of this research to obtain such data for the ternary systems of aniline-isooctane-cumene, aniline-isooctane-xylene and aniline-isooctane-cyclohexane.

Solubility measurements have been carried out for each of these systems at two different temperatures, 20°C. and 30°C. Tie-line data are also obtained for each system at the two temperatures. Effort also has been made to correlate the tie-line data by employing different kinds of plots as presented in the appendix.

The materials used in this research were obtained from several sources. The hydrocarbons were supplied by Phillips Petroleum Company in technical grade with the exception of isooctane which was obtained as purified commercial grade. The xylene used was a mixture of para and meta xylene. Aniline was obtained in reagent grade from Baker Company and from Mathewson Company of St. Louis, Missouri; they were freshly distilled each time before use.

Due to the prevailing water temperature of the season and the lack of expensive equipment, it was very difficult to control the experimental temperatures. However, it can be safely said the accuracy of the temperature control is within ±1°C. of the specified temperature. The density and refractometer determinations are accurate to four significant figures.

THEORY

I. Triangular Phase Diagram

For the purpose of this thesis the phase rule may be simply stated:

$$F = N - P + 2$$

Where F is the number of degrees of freedom of a system, and gives the number of variables whose values must be specified arbitrarily before the state of the system can be completely and unambiguously characterized.

N = number of components, or the lowest number of independent variable constituents required to express the composition of each phase.

P = number of phases.

The phase rule is generally valid under all conditions of distribution provided that equilibrium exists in the system.

For a three component system, the phase rule takes the form

$$F = 3 - P + 2 = 5 - P$$

In such systems a single phase possesses four degree of freedom; namely, pressure, temperature and the compositions of two out of the three components. Such a system is difficult of graphical expression. For this reason, it is customary to present the data in ternary systems at some fixed pressure (atmospheric), and at various constant temperatures. Under these conditions, it is possible to present the concentration relations by the three components at any given temperature on a planar diagram. The most useful presentation is to plot the compositions of the system in triangular coordinates. The apices represent the pure components. Any point along any one of the three

sides represents the binary systems consisting of the two components marked at the ends of the side. Any point inside the triangle represents a mixture of all three components in relative amounts given by the length of the perpendiculars from this point to the three sides. The geometry of the figure requires that the sum of the three percentages adds up to 100.

Although many categories of three component systems are possible and have been observed, only those where immiscibility occurs are of any importance in liquid-liquid extraction, and they may be calssed as follows:

Type 1. Formation of one pair of partially miscible liquids.

Type 2. Formation of two pairs of partially miscible liquids.

Type 3. Formation of three pairs of partially miscible liquids.

Type 4. Formation of solid phases.

Out of these four types only the first two are of any interest in this study, for the systems aniline-isooctane-cumene and aniline-isooctane-xylene belong to the first category, and the system aniline-isooctane-cyclohexane belongs to the second.

A. Type 1. Formation of One Pair of Partially Miscible Liquids.

This is the most common type of the three component systems. A tenary system of this type may be considered as composed of three binary systems, A-B, B-C and A-C, in which two of the three binary systems are completely miscible and the third binary system is only partially miscible with the other two. The systems aniline-isooctane-cumene and aniline-isooctane-xylene are of this type, and they are presented in Figure No. 1 to 4. Referring to Figure No. 1, any mixture whose overall composition is represented by a point in the two phase region (under the curve) will separate into two phases when equilibrium is reached. The compositions of these

two layers, the conjugate layers as they are sometimes called, will lie on opposite sides of the saturated curve. The line which connects the compositions of the two conjugated layers on the saturation curve is called a tie line. The relative weights of the two layers can be calculated analytically from the compositions or graphically from the tie-line segments. The weights of the two layers are inversely proportional to the respective lengths of the tie-line segments. Thus in Figure No. 1, L and N represent the compositions of the isooctane rich and the aniline rich layers respectively, and the relative weight of the two layers may be calculated as follows:

$$\frac{\text{Wt. of isooctane rich layer}}{\text{Wt. of aniline rich layer}} = \frac{\overline{MN}}{\overline{ML}}$$

At point P, which is called the plait point, the compositions of the two layers become the same. Usually the plait point is not located at the maximum point on the solubility curve. It may be determined either by trial and error or by graphical method. In the former method, a certain mixture of A and B is titrated with pure C in a graduated cylinder until the two layers just disappear. If the composition of the binary mixture of A and B used in the right one, the line of demarcation will not move up nor down upon titration with pure C. The graphical method of obtaining the plait point is completely discussed by Treybal(2) and will not be mentioned here.

B. Type 2. Formation of Two Pairs of Partially Miscible Liquids.

In this case, at the temperature of the plot, both the liquid pairs, A-B and B-C, are partially miscible, while C dissolves in any proportion in A. The system aniline-isooctane-cyclohexane is of this type and is presented in Figure Nos. 5 and 6. The area within the band lying across

the triangle represents mixtures which form two liquid layers, the composition of which are at the ends of the tie lines through the points representing the mixtures as a whole.

A complete discussion of the triangular phase diagrams is beyond the scope of this thesis; for this the reader is referred to the standard works of physical chemistry and others dealing specifically with the subject(14),(20).

II. Correlation of Tie-Line Data

In the case of many ternary systems described in literature, only a few tie lines have been experimentally determined. In order to obtain further data without recourse to experiment, interpolation is necessary. Direct interpolation from the triangular diagram is unsatisfactory, however, several indirect methods of dealing with the problem have been devised.

A. Horizontal Tie-Line Method.

According to Hand(9) the tie lines for ternary systems of one consolute and two immiscible liquids become horizontal when the systems are plotted with properly selected units for one of the immiscible liquids. This is done by altering the unit of one of the immiscible liquids so as to bring the plait point to the maximum point on the solubility curve.

B. Graphical Interpolation on the Triangular Plot.

Lines can be drawn from conjugate points of a tie line parallel, respectively, to the two sides of the triangle and intersecting at a point. A tie-line curve may then be drawn through all the points obtained by repeating the procedure for other known tie lines. Since this method requires extension below the base line of the triangle, therefore it cannot be done conveniently on the triangular graph paper ordinarily available. A modification of the method has been proposed by Sherwood(15) in which a

line is drawn from one conjugate point parallel to the base to intersect a second line drawn from the other conjugate point parallel to the side of the triangle. A curve can be drawn through a series of such points forming a conjugate curve from which other tie lines may be interpolated. However, these methods require a considerable amount of tie-line data; therefore, it is desirable to develop a method to correlate the tie-line data so that they fall in a straight line. In such a case only two accurately known tie lines are required.

C. Bachman Plot.

If A and B are the nonconsolute components of a ternary system, then a plot of weight percent of A in A-rich layer against the weight percent of B in B-rich layer will produce a smooth tie-line curve. The equation of this curve is

$$X_{AA}X_{BB} = aX_{AA} + bX_{BB}$$

where

X_{AA} = Wt. percent of A in A-rich layer
X_{BB} = Wt. percent of B in B-rich layer

a and b are constants

If the equation is written in the form

$$X_{AA} = a\frac{X_{AA}}{X_{BB}} + b$$

A-rich layer is plotted against the ratio of weight percent of A in A-rich layer to the weight percent of B in B-rich layer, a straight line will result. This method is limited to those systems which contain only one pair of nonconsolute liquids. For systems such as aniline-isooctane-cyclohexane, a smooth curve is the result.

Brown(6) states that straight-line Bachman plots are obtained for double nonconsolute pair systems only when the ratio to be plotted is correctly chosen. Brown(6) pointed out that, in every case, Bachman(1) arbitrarily selected the solvent phase as the numerator in the ratio plotted. In such a case only for the single nonconsolute pair type system is a linear plot obtained. Brown(6) altered the Bachman ratio so that the solvent is in the denominator. He illustrated this by plotting the ratio of per cent N-heptane in hydrocarbon layer to the per cent of aniline in solvent phase against per cent N-heptane in hydrocarbon layer for the aniline-n-heptane-cyclohexane system. A straight line is obtained in such a case.

D. Conway-Phillip(7) Method.

By studying the furfural-ethyl acetate-water system and a few other systems, Conway and Phillip(7) found that if a plot was made of the logarithm of the weight per cent of water in water-layer against the weight per cent of solvent in solvent phase, a straight line would be obtained in a system containing two partially miscible pairs. They pointed out, however, that the method is not applicable to the aniline-n-heptane-methylcyclohexane system.

E. Othmer and Tobias(11) Method.

Othmer and Tobias(11) developed what is called a modification of Bachman's equation. The following derivation of the equation is extracted from the paper of Othmer and Tobias(11). Bachman's equation may be written as

$$\frac{X_{AA}}{X_{BB}} = aX_{AA} - b \qquad (1)$$

In ternary systems with practically immiscible nonconsolute components, the value of X_{AA} and X_{BB} for the tie line with zero solute would be approximately equal to 1. Then

$$-b = 1 - a \qquad (2)$$

substituting this in equation (1) and rearranging

$$X_{AA} = aX_{AA}X_{BB} + X_{BB}(1 - a) \qquad (3)$$

Subtracting $X_{AA}X_{BB}$ from each side of equation (3) and factoring gives

$$\frac{\frac{1 - X_{AA}}{X_{AA}}}{\frac{1 - X_{BB}}{X_{BB}}} = 1 - a = -b \qquad (4)$$

Since $a + b + c = 1$ in each liquid phase, equation (4) is written as

$$\frac{\frac{X_{BA} + X_{CA}}{X_{AA}}}{\frac{X_{AB} + X_{CB}}{X_{BB}}} = 1 - a = -b \qquad (5)$$

which is also expressed as

$$\frac{X_{BA} + X_{CA}}{X_{AA}} = (1 - a)\frac{(X_{AB} + X_{CB})}{X_{BB}}$$

Take logarithm of both sides

$$\log\frac{X_{BA} + X_{CA}}{X_{AA}} = \log\frac{X_{AB} + X_{CB}}{X_{BB}} = \log(1 - a)$$

This equation will give a linear plot for tie-line data of ternary systems where the nonconsolute components are immiscible. A more general equation which may be obtained by applying the suggestion of Hand's revised Nerst equation

$$\frac{X_{CA}}{X_{AA}} = K\left(\frac{X_{CB}}{X_{BB}}\right)^n \quad \text{to equation (7).}$$

Thus, if an additional parameter exponent n is applied to the first term on the right-hand side of equation (7), the following equation is obtained.

$$\log \frac{X_{BA} + X_{CA}}{X_{AA}} = \log \left(\frac{X_{AB} + X_{CB}}{X_{BB}} \right)^n + S = n \log \frac{X_{AB} + X_{CB}}{X_{BB}} + S$$

where S is a constant.

Since $1 - X_{AA} = X_{BA}$ and $1 - X_{BB} = X_{AB} + X_{CB}$

$$\log \frac{1 - X_{AA}}{X_{AA}} = n \log \frac{1 - X_{BB}}{X_{BB}} + S$$

Therefore, a plot on logarithmic coordinates of the ratio of one minus the fraction of solvent in solvent-rich layer to the fraction of solvent in solvent-rich layer against the ration of one minus the fraction of diluent in diluent-rich layer to the fraction of diluent in diluent-rich layer, a straight line will result.

III. Experimental Determination of the Ternary-Equilibrium Data.

If chemical analysis for two of the three components in the system is readily carried out, both tie lines and binodal curve may be determined simultaneously. Refer to Figure No. 1. If a mixture of composition M is shaken in a constant water bath corresponding to that of the diagram, then on standing, two layers at L and N will form. The two layers can then be separated and analyzed for the two components. Repetition of this procedure will give a complete knowledge of the diagram. In the case of this research, the analysis of the three components involved is difficult. However, it is possible to determine a physical property of the mixtures along the binodal curve which will vary sufficiently with concentration so that it can be used for analytical purposes. The refractive index is used in this research on account of the

fact that it is easily and accurately measured. Thus, referring to Figure No. 1, the determination of the refractive indices of the layers L and N, and reference to a plot of refractive index against percentage compositions of isooctane or aniline along the binodal curve will fix the position of L and N.

NOMENCLATURE

A = component of a solution

a = constant

B = component of a solution

b = constant

C = component of a solution

F = degree of freedom

K = constant

N = number of components

n = constant

P = number of phases in equilibrium

X = concentration, weight fraction

Subscripts:

A, B C refer to components A, B, C respectively.

EXPERIMENTAL PROCEDURE

I. Determination of Specific Gravity

The specific gravities of all chemicals used are determined both at 20°C. and at 30°C. by use of a pycnometer equipped with a cap and a thermometer. The net weight of the pycnometer (including the cap and thermometer) is first determined by use of an analytical balance. Water is then introduced into the pycnometer and is weighed at 20°C. and at 30°C. The difference between the total weight (water and tare) at a certain temperature and the tare is the net weight of water at that temperature. The weights of other chemicals are also obtained in the same manner as for water. The ratio of the weight of the chemical in question held by the pycnometer at a certain temperature to the weight of water contained by the pycnometer at the same temperature is the specific gravity of the chemical at the temperature referred to. The determination of specific gravities is necessary because the amount of each constituent used in each system is determined from the volume introduced and the density.

II. Determination of Solubility Curves

A. Systems forming one pair of immiscible liquids

The solubility curve is determined by using a method exactly opposite to that of the much used cloud point method. The reason is that it is easier to detect the end point of the titration by going from the two-phase region. Mixtures of different proportions of isooctane and aniline are prepared in flasks of adequate capacity and are kept in a constant water bath. Enough time is allowed for the mixture to come to the temperature of the bath before

they are titrated by the third component (cumene or xylene). The titration is carried out with vigorous stirring until the cloudiness just disappears. The solution is kept in the water bath after titration for about 15 minutes. If the solution remains clear at the end of 15 minutes, the end point is reached. If the solution returns to cloudy during this period, repeat the titration until the solution becomes clear again. This is based upon the fact that when there are two liquid phases present, the mixture will appear cloudy upon agitation, and the cloudiness will disappear when there is only one liquid phase. After all the titrations are completed, the amount of each constituent used in each titration is calculated from the volume introduced and the density. The points thus obtained are plotted on triangular coordinates. After each titration is completed, the refractive index of the resulting solution is determined by means of an Abbe Spencer refractometer. The refractive indices are plotted against the percentage compositions of isooctane and against the compositions of aniline on rectangular coordinates. The resulting curves are to be used for the analysis of the conjugate liquids for the determination of tie-line data.

B. Systems forming two pairs of immiscible liquids

The aniline-isooctane-cyclohexane systems forms two pairs of immiscible liquids; therefore, the procedure developed for the aniline-isooctane-cumene or xylene systems is inadequate and has to be modified to suit the present system.

Binary mixtures of cyclohexane and isooctane in different proportions are prepared in duplicate and are kept in the constant water bath. One of the two samples with the same proportion of isooctane to cyclohexane is titrated with aniline until the solution becomes slightly cloudy. The

other sample is titrated through the cloud point and through the two phase region until the solution just becomes clear again. The duplicate sample serves two purposes; that is to check the first point and to locate a point on the second solubility curve. Refractive indices are taken for each of the two solutions and are plotted against per cent of isooctane or per cent of aniline and against per cent of aniline respectively. Two curves are thus obtained; one for the isooctane-rich layer and one for the aniline-rich layer.

III. Determination of Tie Lines

The tie lines were determined by shaking mixtures of known composition at constant temperature for eight hours, allowing the layers to separate at the same temperature and removing the two layers. The refractive index of each layer is separately determined. Referring to the plots of refractive index against the percentage composition of any component along the solubility curve, will fix the positions of the conjugated liquids.

IV. Precision of Data

The densities and the refractive indices obtained in this experiment are accurate to the fourth significant figure. However, the temperature control is accurate within $\pm 1^{\circ}$ of the specified temperature. All calculations are performed with a slide rule and are therefore accurate to three significant figures.

CONCLUSION

With reference to Figure No. 1 to 5, it is easily seen that aniline may be used as solvent in the extraction of aromatics from paraffins in the purification of petroleum fraction, because of its preferential solubility for the former and the substantial immiscibility with the latter, especially at lower temperature. In any successful liquid-liquid extraction process, the extracting solvent and the solution to be extracted should be highly immiscible. This means that high concentration of distributed solute can be attained before complete solution of the immiscible liquid occurs. This would increase the ultimate extent of separation possible. From the slopes of the tie lines and the tine-line data, it is obvious that the distribution coefficient is less than unity, which means that the distribution favors the isooctane-rich phase and that isooctane is more selective in separating solutions of aromatics and isooctane. For this reason, a large amount of solvent may have to be used to obtain the desired separation.

The selectivity S of aniline for aromatic compounds may be definsed as follows:

$$S = \frac{X_{CB}X_{BB}}{X_{CA}X_{BA}} = m\frac{X_{BB}}{X_{BA}}$$

where

X_{CA} = concentration of aromatics in isooctane-rich phase

X_{CB} = concentration of aromatics in aniline-rich phase

X_{BB} = concentration of aniline in aniline-rich phase

X_{BA} = concentration of aniline in isooctane-rich phase

Although the distribution coefficient m is smaller than unity in each case, but the slopes of the tie lines are not too steep, with the exception of the cyclohexane-isooctane-aniline system; hence, the distribution coefficients do not deviate too much from unity. Since the ratios $\frac{X_{BB}}{X_{BA}}$ are much larger than unity, with the exception of points near the plait point, the selectivities are larger than unity for every system. Practical process requires that S should exceed unity, the more so the better.

In conclusion, aniline can be used successfully as solvent for separating solutions containing aromatic compounds and paraffins. The process should be carried out at as low a temperature as possible, because of increasing immiscibility. Aniline is a better solvent for separating solutions of isooctane and cumene than solutions of xylene and cumene, and solutions of cyclohexane and aniline on account of the larger distribution coefficients and selectivities. The recovery of aniline from the extract may be carried out by distillation or evaporation because of the great difference in boiling point between the aniline and the aromatics considered. However, the only draw back is that the distribution favors the isooctane-rich phase and, hence, large amounts of solvent may have to be used to insure a satisfactory separation.

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APPENDIX

TABLE 1

EXPERIMENTAL DATA OF ISOOCTANE-ANILINE-CUMENE SYSTEM AT 20°C.

ISOOCTANE			ANILINE			CUMENE			REFRACTIVE INDEX
c.c.	Gm.	%	c.c.	Gm.	%	c.c.	Gm.	%	
25	17.97	32.3	25	20.43	46.0	14.2	12.1	21.8	1.4923
25	17.97	36.2	20	20.43	41.2	13.1	11.17	22.5	1.4840
25	17.97	41.4	15	15.32	35.3	11.05	10.1	23.3	1.4750
25	17.97	49.5	10	10.22	28.1	9.55	8.14	22.4	1.4616
25	17.97	62.3	5	5.11	17.7	6.78	5.77	20.0	1.4425
30	21.55	66.9	5	5.11	15.87	6.50	5.54	17.22	1.4373
35	25.55	71.9	5	5.11	14.4	5.70	4.86	13.68	1.4340
40	38.75	78.23	5	5.11	10.32	6.65	5.67	11.45	1.4305
20	14.27	28.5	25	25.55	50.90	12.15	10.35	20.6	1.5003
15	10.78	23.95	25	25.55	56.7	10.22	8.71	19.35	1.5100
10	7.18	18.43	25	25.55	65.6	7.3	6.22	15.97	1.5280
5	3.59	11.18	25	25.55	79.6	3.5	2.98	9.28	1.5478

TABLE 2

EXPERIMENTAL DATA OF CUMENE-ISOOCTANE-ANILINE SYSTEM AT 30°C.

ISOOCTANE			ANILINE			CUMENE			REFRACTIVE INDEX
c.c.	Gm.	%	c.c.	Gm.	%	c.c.	Gm.	%	
25	17.92	34.1	25	25.35	48.3	10.8	9.27	17.65	1.48920
25	17.92	38.2	20	20.3	43.2	10.2	8.75	18.6	1.4818
25	17.92	51.7	10	15.2	29.2	7.8	6.63	19.1	1.4580
25	17.92	66.4	5	10.14	18.8	4.65	3.99	14.8	1.4381
30	21.5	70.75	5	5.07	16.68	4.45	3.82	12.57	1.4320
40	28.7	77.6	5	5.07	13.7	3.75	3.22	8.7	1.4232
20	14.35	29.9	25	25.35	52.8	9.70	8.25	17.2	1.4990
10	7.17	19.4	25	25.35	68.5	6.25	4.47	12.1	1.5252
5	3.585	11.9	25	25.35	83.9	1.5	1.276	4.2	1.5498
25	17.92	43.8	15	15.2	37.2	9.15	7.78	19.0	1.4712
69	49.45	90.7	5	5.07	9.3	0	0	0	1.4108

TABLE 3

EXPERIMENTAL DATA OF ISOOCTANE-ANILINE-XYLENE SYSTEM AT 20°C.

ISOOCTANE			ANILINE			XYLENE			REFRACTIVE INDEX
c.c.	Gm.	%	c.c.	Gm.	%	c.c.	Gm.	%	
25	17.92	32.5	25	25.35	46.0	12.64	11.86	21.5	1.4922
25	17.92	37.3	20	20.3	42.3	11.42	9.8	20.4	1.4840
25	17.92	42.7	15	15.2	36.2	10.32	8.86	21.1	1.4740
25	17.92	50.7	10	10.14	28.7	8.5	7.3	20.6	1.4605
25	17.92	64.1	5	5.07	18.1	5.80	4.98	17.8	1.4410
40	28.7	72.8	5	5.07	12.9	6.55	5.62	14.3	1.4302
75	53.76	85.4	5	5.07	8.05	4.74	4.10	6.6	1.4177
110	78.9	94.0	5	5.07	6.0	0	0	0	1.4092
20	14.35	29.4	25	25.35	52.0	10.6	9.1	18.6	1.5008
10	7.17	18.7	25	25.35	66.2	6.73	5.78	15.1	1.5255
5	3.585	11.3	25	25.35	80.0	3.23	2.775	8.7	1.5487

TABLE 4

EXPERIMENTAL DATA OF ISOOCTANE-ANILINE-XYLENE SYSTEM AT 30°C.

ISOOCTANE			ANILINE			XYLENE			REFRACTIVE INDEX
c.c.	Gm.	%	c.c.	Gm.	%	c.c.	Gm.	%	
25	17.92	34.5	25	25.4	49.0	10.0	8.59	16.55	1.4900
25	17.92	39.2	20	20.3	44.4	8.7	7.475	16.4	1.4811
25	17.92	45.0	15	15.2	38.2	7.8	6.7	16.8	1.4704
25	17.92	54.2	10	10.14	30.6	5.84	5.02	15.2	1.4556
25	17.92	68.7	5	5.07	19.43	3.60	3.095	11.87	1.4342
30	21.5	72.9	5	5.07	17.2	3.43	2.95	10.0	1.4295
40	28.7	78.9	5	5.07	13.92	3.05	2.62	7.2	1.4225
20	14.34	30.5	25	25.4	54.0	8.45	7.26	15.5	1.4980
10	7.17	19.4	25	25.4	68.9	5.0	4.3	11.7	1.5250
5	3.585	11.84	25	25.4	83.9	1.5	1.29	4.26	1.5490

TABLE 5

EXPERIMENTAL DATA OF CYCLOHEXANE-ISOOCTANE-ANILINE SYSTEM AT 20°C.

CYCLOHEXANE			ISOOCTANE			ANILINE			REFRACTIVE INDEX
c.c.	Gm.	%	c.c.	Gm.	%	c.c.	Gm.	%	
25	19.1	87.85	0	0	0	2.6	2.64	12.15	1.4350
5	3.82	18.6	0	0	0	16.5	16.72	81.4	1.5455
25	19.1	75.7	5	3.585	14.2	2.5	2.54	10.1	1.4296
5	3.82	12.92	1	0.717	2.43	24.62	25.0	84.65	1.5513
25	19.1	58.5	15	10.76	33.0	2.75	2.79	8.5	1.4225
5	3.82	8.03	3	2.15	4.53	41.05	41.6	87.45	1.5562
25	19.1	47.4	25	17.92	44.4	3.25	3.3	8.2	1.4205
5	3.82	5.69	3	2.15	5.34	35.3	35.8	89.0	1.5587
15	11.46	36.1	25	17.92	56.4	2.35	2.38	7.5	1.4175
3	2.29	3.81	5	3.585	5.96	53.8	54.3	90.23	1.5622
5	3.82	16.3	25	17.92	76.4	1.7	1.724	7.34	1.4133
1	0.764	1.433	5	3.585	6.72	48.3	49.0	91.9	1.5655
0	0	0	25	17.92	93.63	1.2	1.218	6.37	1.4092
0	0	0	5	3.585	7.03	46.7	47.4	92.97	1.5680

TABLE 6

EXPERIMENTAL DATA OF CYCLOHEXANE-ISOOCTANE-ANILINE SYSTEM AT 30°C.

CYCLOHEXANE			ISOOCTANE			ANILINE			REFRACTIVE INDEX
c.c.	Gm.	%	c.c.	Gm.	%	c.c.	Gm.	%	
25	19.1	76.9	0	0	0	5.65	5.73	23.1	1.4462
5	3.82	27.0	0	0	0	10.2	10.35	73.0	1.5282
25	19.1	68.3	5	3.585	12.8	5.225	5.3	18.92	1.4375
5	3.82	19.1	1	0.717	3.585	15.25	15.47	77.3	1.5351
25	19.1	54.4	15	10.76	30.6	5.20	5.275	15.0	1.4289
5	3.82	11.18	3	2.15	6.3	27.80	28.2	82.5	1.5438
25	19.1	45.0	25	17.92	42.3	5.30	5.375	12.7	1.4241
3	2.29	8.06	3	2.15	7.57	23.6	23.95	84.4	1.5492
15	11.46	34.4	25	17.92	53.7	3.90	3.96	11.86	1.4205
3	2.29	5.15	5	3.585	8.05	38.2	38.7	86.8	1.5514
5	3.82	15.72	25	17.92	73.73	2.5	2.535	10.45	1.4148
1	0.764	1.89	5	3.585	8.87	35.63	36.1	89.4	1.5565
0	0	0	25	17.92	90.7	1.82	1.845	9.33	1.4106
0	0	0	5	3.585	9.21	34.8	35.3	90.8	1.5590

TABLE 7

TIE-LINE DATA OF CUMENE-ISOOCTANE-ANILINE SYSTEM AT 20°C.

REFRACTIVE INDEX		COMPOSITION IN PER CENT BY WEIGHT					
HYDROCARBON-RICH PHASE	ANILINE-RICH PHASE	HYDROCARBON-RICH			ANILINE-RICH		
		ISOOCTANE	ANILINE	CUMENE	ISOOCTANE	ANILINE	CUMENE
1.4355	1.5393	68.25	15.4	16.3	14.1	73.8	12.1
1.4580	1.5175	51.8	26.3	21.9	21.1	61.1	17.8
1.4150	1.5575	86.0	7.3	6.7	9.2	84.75	6.05
1.4245	1.5494	77.4	10.8	11.8	11.0	79.8	9.2
1.4277	1.5465	74.7	12.2	13.1	11.7	78.2	10.1
1.4220	1.5530	79.65	10.0	10.35	10.1	82.0	7.9
1.4180	1.5544	83.2	8.5	8.3	9.9	82.7	7.4

TABLE 8

TIE-LINE DATA OF CUMENE-ISOOCTANE-ANILINE SYSTEM AT 30°C.

REFRACTIVE INDEX		COMPOSITION IN PER CENT BY WEIGHT					
HYDROCARBON-RICH PHASE	ANILINE-RICH PHASE	HYDROCARBON-RICH			ANILINE-RICH		
		ISOOCTANE	ANILINE	CUMENE	ISOOCTANE	ANILINE	CUMENE
1.4265	1.5407	74.9	15.0	10.1	14.0	79.0	7.0
1.4332	1.5344	69.0	17.8	13.2	16.2	74.3	9.5
1.4530	1.5141	54.4	27.3	18.3	23.2	62.2	14.6
1.4210	1.5453	79.8	12.7	7.5	12.5	82.4	5.1

TABLE 9

TIE-LINE DATA OF XYLENE-ISOOCTANE-ANILINE SYSTEM AT 30°C.

REFRACTIVE INDEX		COMPOSITION IN PER CENT BY WEIGHT					
HYDROCARBON-RICH PHASE	ANILINE-RICH PHASE	HYDROCARBON-RICH			ANILINE-RICH		
		ISOOCTANE	ANILINE	XYLENE	ISOOCTANE	ANILINE	XYLENE
1.4185	1.5460	82.7	12.0	5.3	12.8	82.2	5.0
1.4280	1.5372	74.2	16.4	9.4	15.8	76.4	7.8
1.4344	1.5311	69.0	19.4	11.6	13.1	72.6	9.3
1.4400	1.5260	64.8	22.3	12.9	20.0	69.5	10.5

TABLE 10

TIE-LINE DATA OF XYLENE-ISOOCTANE-ANILINE SYSTEM AT 20°C.

REFRACTIVE INDEX		COMPOSITION IN PER CENT BY WEIGHT					
HYDROCARBON-RICH PHASE	ANILINE-RICH PHASE	HYDROCARBON-RICH			ANILINE-RICH		
		ISOOCTANE	ANILINE	XYLENE	ISOOCTANE	ANILINE	XYLENE
1.4169	1.5553	86.8	7.5	5.7	9.2	84.8	6.0
1.4232	1.5511	79.6	10.2	10.2	10.2	82.4	7.4
1.4315	1.5467	72.0	13.8	14.2	11.3	79.7	14.0
1.4130	1.5570	90.0	6.7	3.3	8.8	85.7	5.5

TABLE 11

TIE-LINE DATA OF CYCLOHEXANE-ANILINE-ISOOCTANE SYSTEM AT 20°C.

REFRACTIVE INDEX		COMPOSITION IN PER CENT BY WEIGHT					
		HYDROCARBON-RICH			ANILINE-RICH		
HYDROCARBON-RICH PHASE	ANILINE-RICH PHASE	ISOOCTANE	ANILINE	CYCLO-HEXANE	ISOOCTANE	ANILINE	CYCLO-HEXANE
1.4309	1.5478	10.5	10.5	79.0	1.0	82.7	16.3
1.4286	1.5503	17.0	9.8	73.2	2.3	84.1	13.6
1.4162	1.5592	63.2	7.6	29.2	5.3	89.0	5.7
1.4131	1.5595	76.25	7.0	16.75	5.4	89.14	5.5

TABLE 12

TIE-LINE DATA OF CYCLOHEXANE-ANILINE-ISOOCTANE SYSTEM AT 30°C.

REFRACTIVE INDEX		COMPOSITION IN PER CENT BY WEIGHT					
		HYDROCARBON-RICH			ANILINE-RICH		
HYDROCARBON-RICH PHASE	ANILINE-RICH PHASE	ISOOCTANE	ANILINE	CYCLO-HEXANE	ISOOCTANE	ANILINE	CYCLO-HEXANE
1.4350	1.5328	17.4	17.6	65.0	2.3	75.9	21.8
1.4268	1.5408	35.6	14.2	50.2	5.25	80.75	14.0
1.4177	1.5481	62.9	11.2	25.9	7.3	85.0	7.7
1.4134	1.5525	76.3	10.3	13.4	8.2	87.4	4.4

TABLE 13

SPECIFIC GRAVITIES

REAGENT	SPECIFIC GRAVITY	
	20°C.	30°C.
CUMENE	0.8620	0.8560
XYLENE	0.8644	0.8589
CYCLOHEXANE	0.7740	0.7673
ANILINE	1.0231	1.0182
ISOOCTANE	0.7267	0.7202

FIGURE 1

TRIANGULAR PHASE DIAGRAM

OF

CUMENE-ISOOCTANE-ANILINE SYSTEM

AT 20°C.

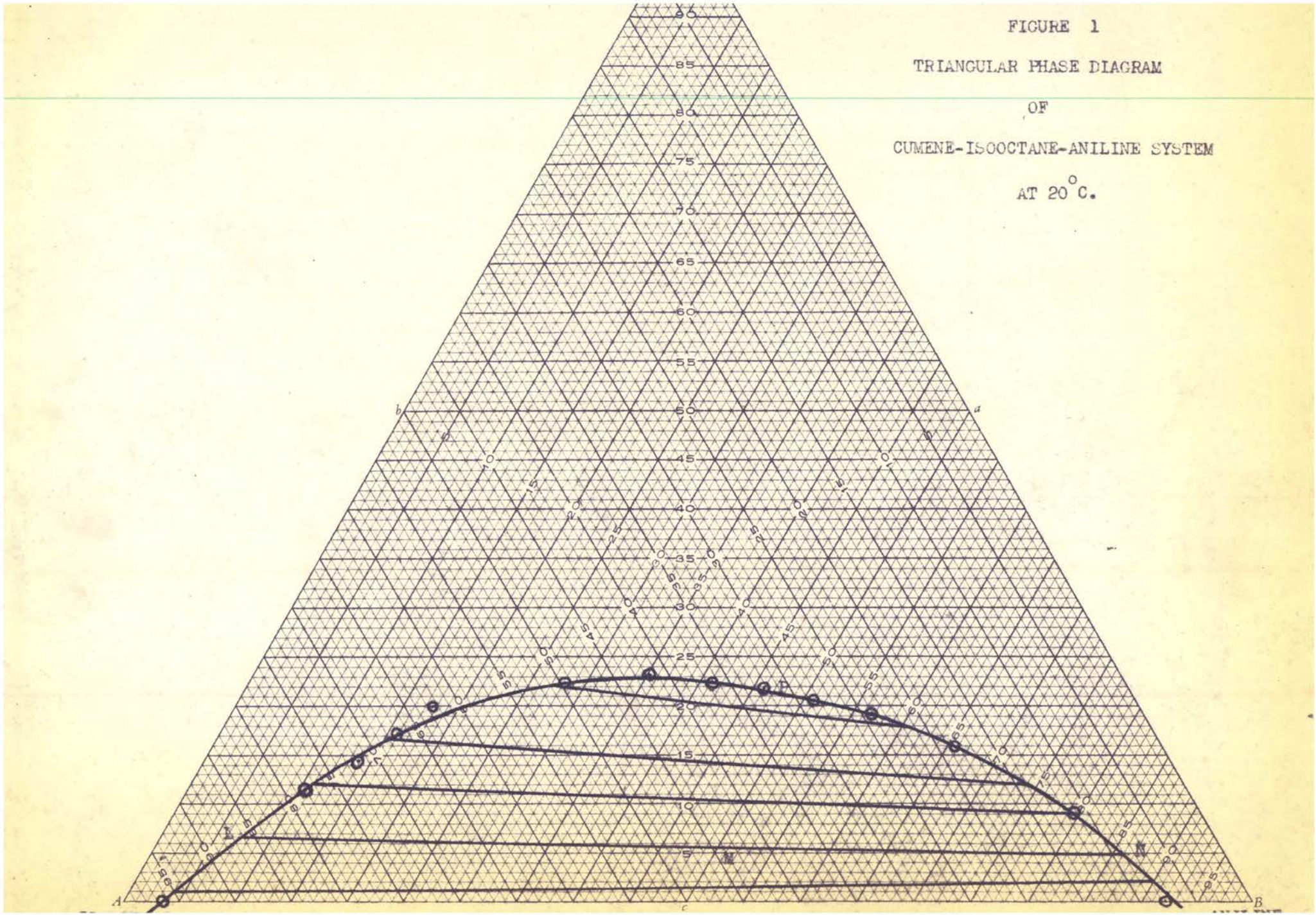


FIGURE 2

TRIANGULAR PHASE DIAGRAM

CUMENE-ISOOCTANE-ANILINE SYSTEM

AT 30°C.

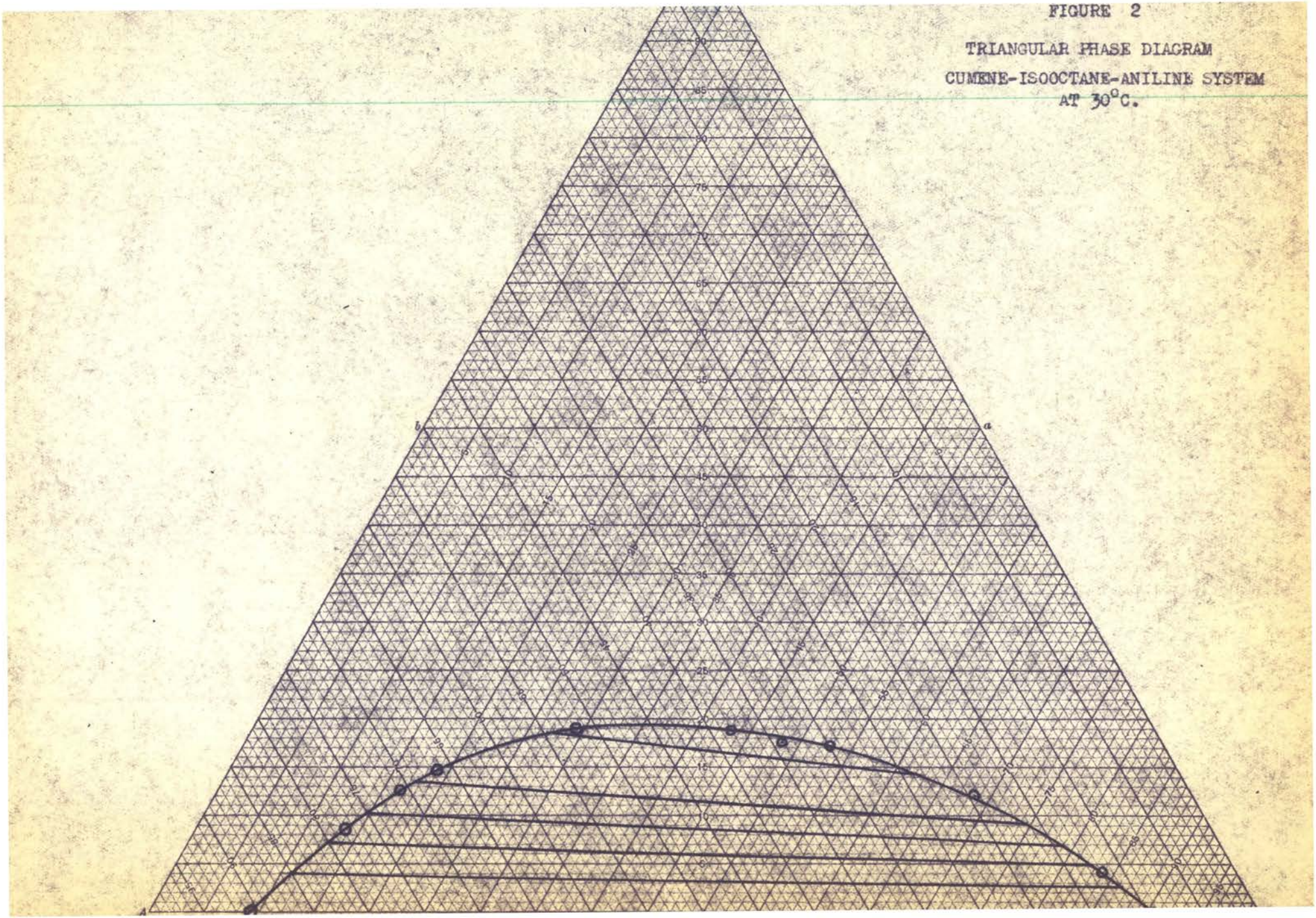


FIGURE 3

TRIANGULAR PHASE DIAGRAM OF

XYLENE-ANILINE-ISOOCTANE

SYSTEM AT 20°C.

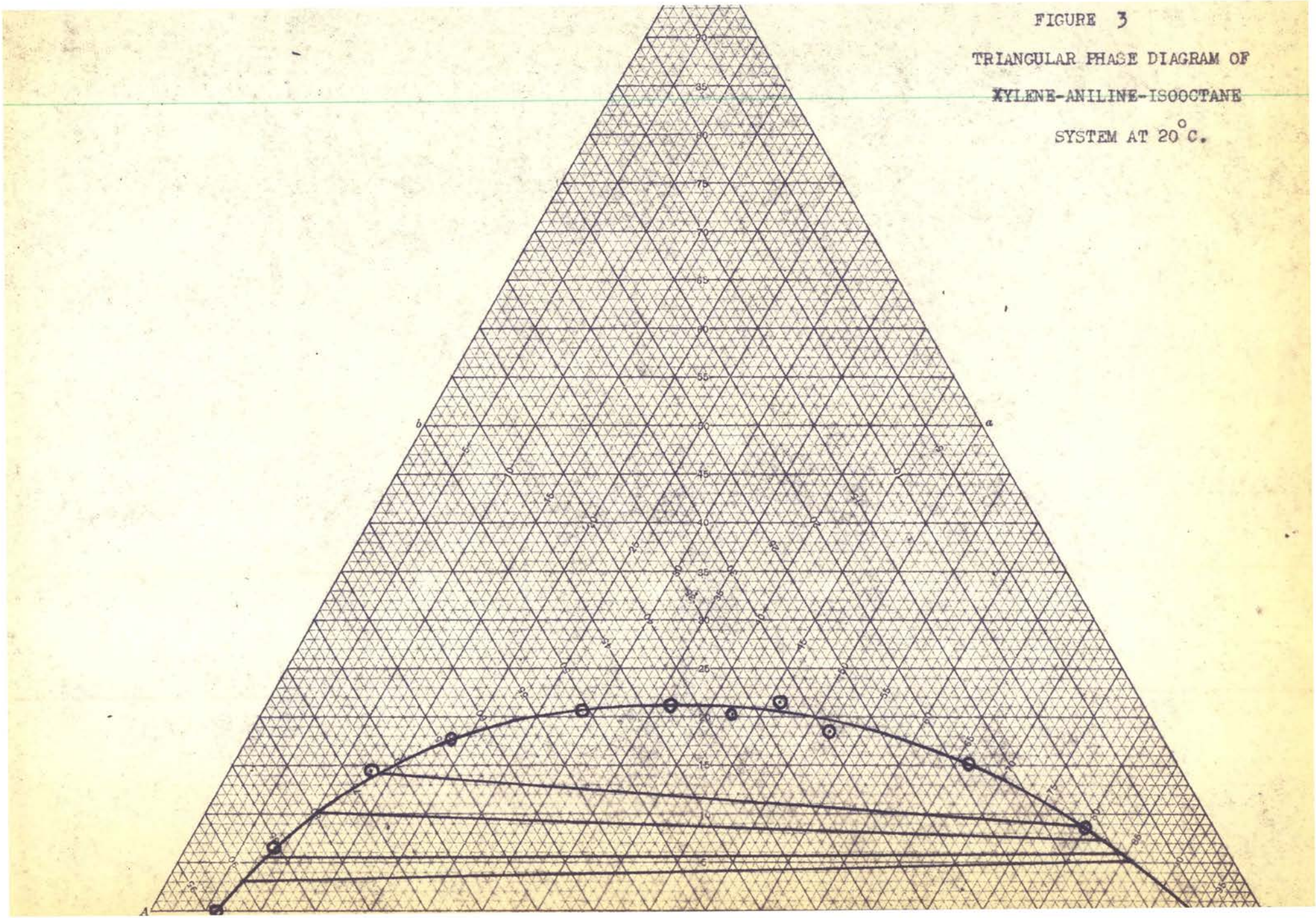


FIGURE 4

TRIANGULAR PHASE DIAGRAM

XYLENE-ISOOCTANE-ANILINE

SYSTEM AT 30°C.

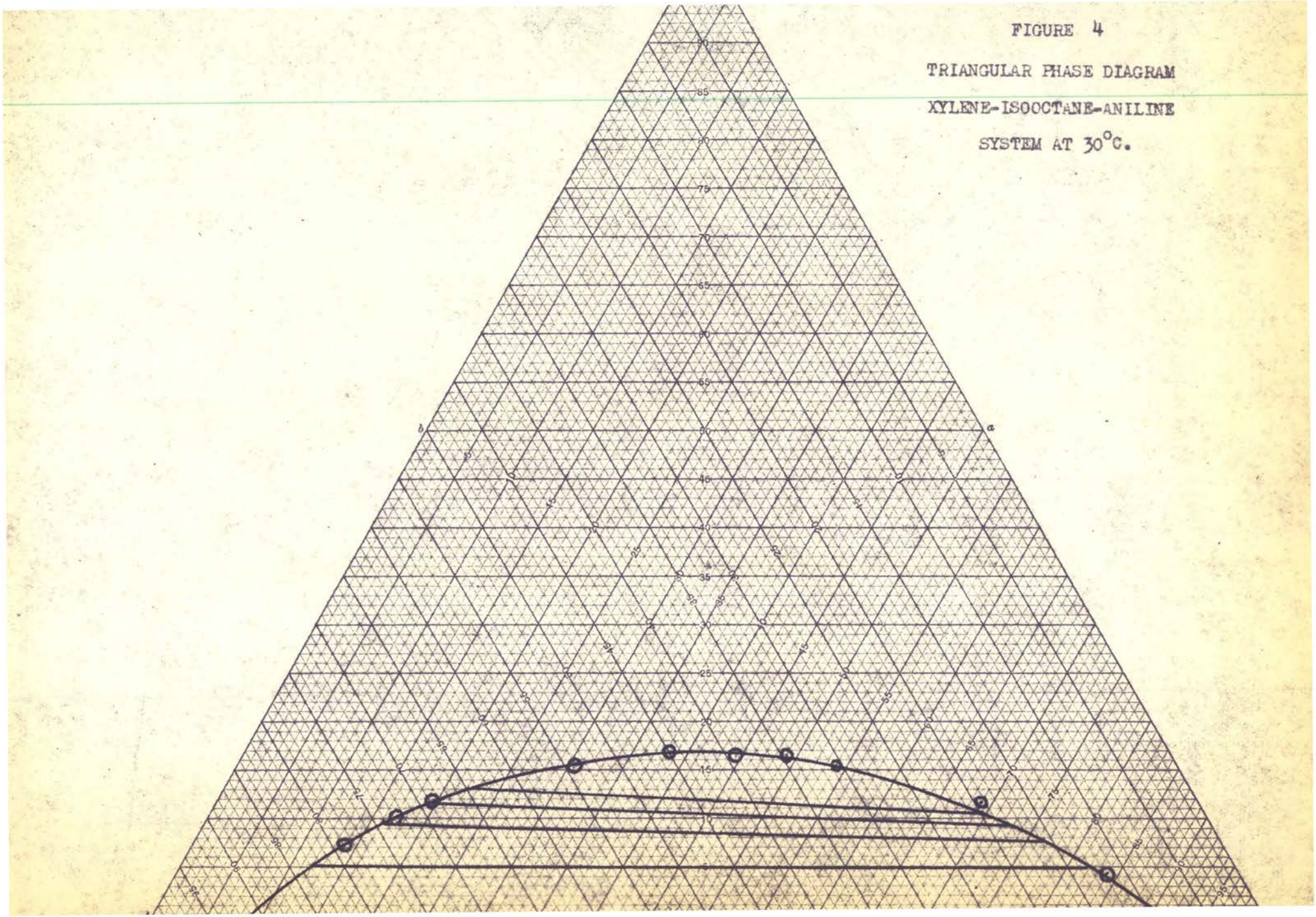


FIGURE 5

TRIANGULAR PHASE DIAGRAM FOR CYCLOHEXANE-ISOOCTANE-ANILINE SYSTEM AT 20°C.

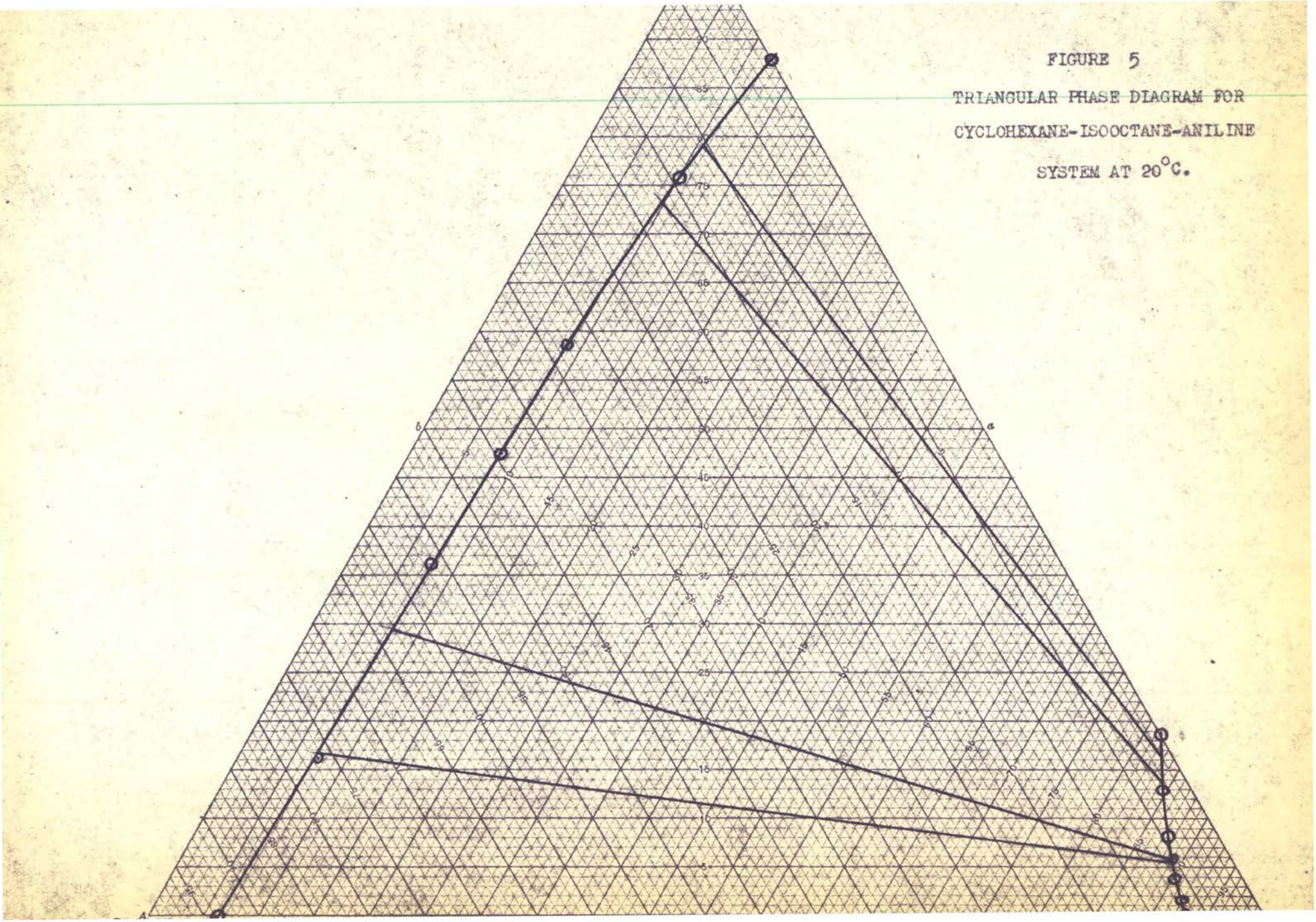


FIGURE 6

TRIANGULAR PHASE DIAGRAM FOR CYCLOHEXANE-ISOOCTANE-ANILINE SYSTEM AT 30°C.

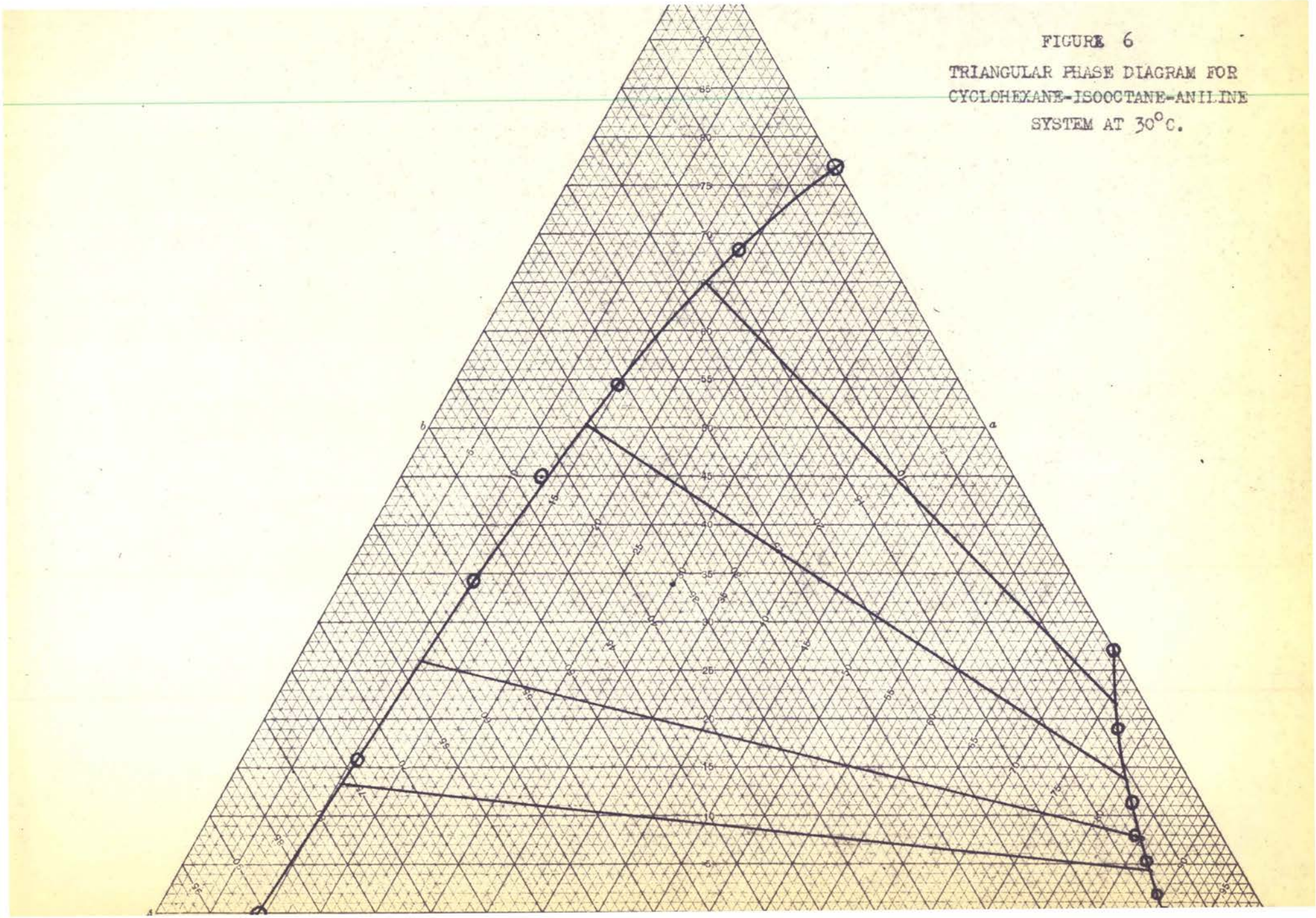


FIGURE 7

BACHMAN PLOT OF TIE-LINE DATA

FOR CUMENE-ANILINE-ISOOCTANE

SYSTEM AT 20°C.

$\frac{\text{\% ISOOCTANE IN ISOOCTANE-RICH PHASE}}{\text{\% ANILINE IN ANILINE-RICH PHASE}}$

VS.

% ISOOCTANE IN ISOOCTANE-RICH PHASE

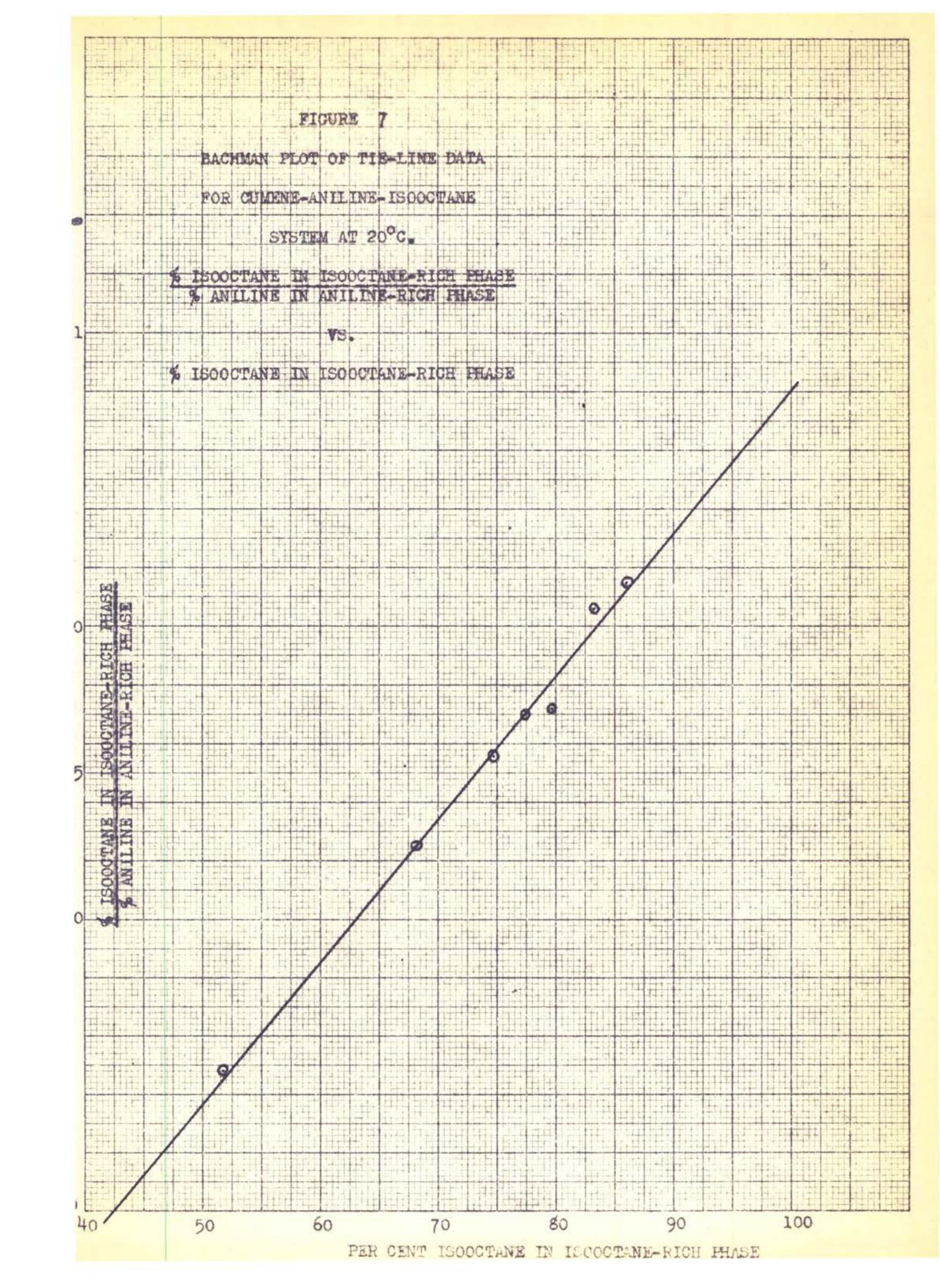


FIGURE 8

BACHMAN PLOT OF TIE-LINE DATA FOR CUMENE-ISOOCTANE-ANILINE SYSTEM AT 30°C.

RATIO OF PER CENT OF ISOOCTANE IN ISOOCTANE-RICH LAYER TO PER CENT OF ANILINE IN ANILINE-RICH LAYER

VS.

PER CENT ISOOCTANE IN ISOOCTANE-RICH LAYER

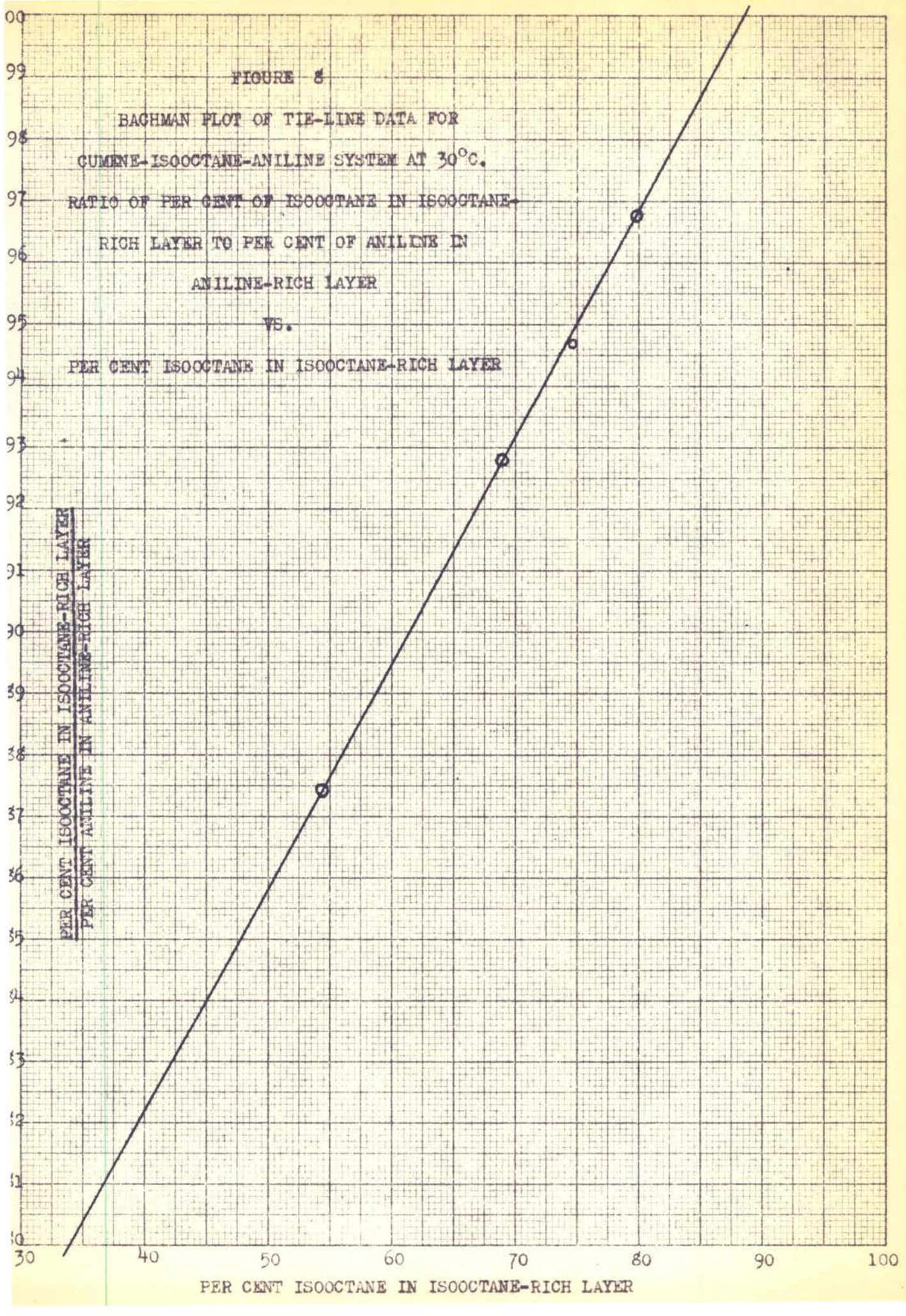


FIGURE 9

BACHMAN PLOT OF TIE-LINE DATA FOR XYLENE-ISOOCTANE-ANILINE SYSTEM AT 20°C.

RATIO OF PER CENT OF ISOOCTANE IN ISOOCTANE-RICH LAYER TO PER CENT OF ANILINE IN ANILINE-RICH LAYER

VS.

PER CENT ISOOCTANE IN ISOOCTANE-RICH LAYER

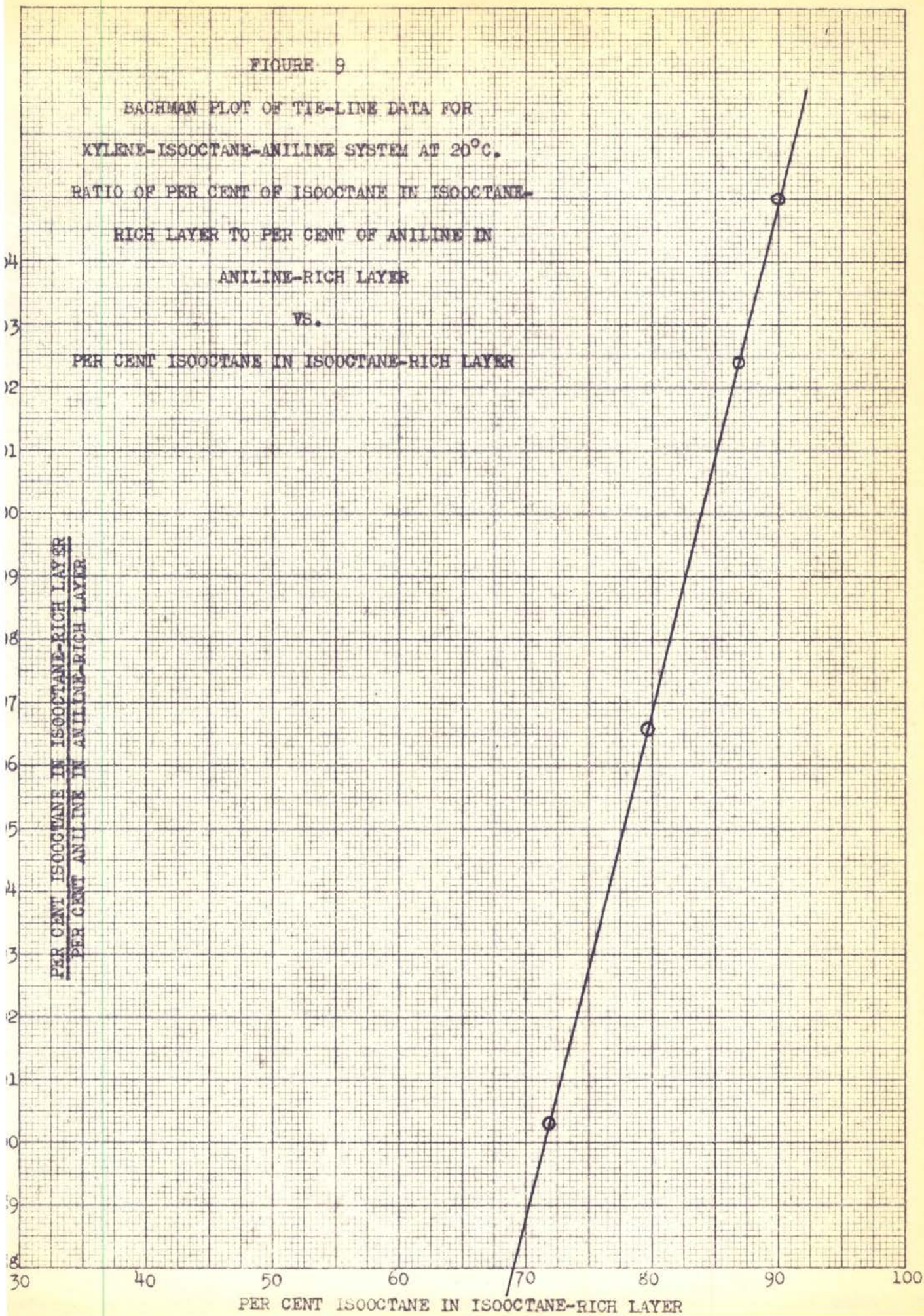


FIGURE 10

TIE-LINE CORRELATION DIAGRAM FOR XYLENE-ISOOCTANE-ANILINE SYSTEM AT 30°C.

RATIO OF WEIGHT PER CENT OF ISOOCTANE IN ISOOCTANE-RICH LAYER TO WEIGHT PER CENT OF ANILINE IN ANILINE-RICH LAYER

VS.

PER CENT OF ISOOCTANE IN ISOOCTANE-RICH LAYER

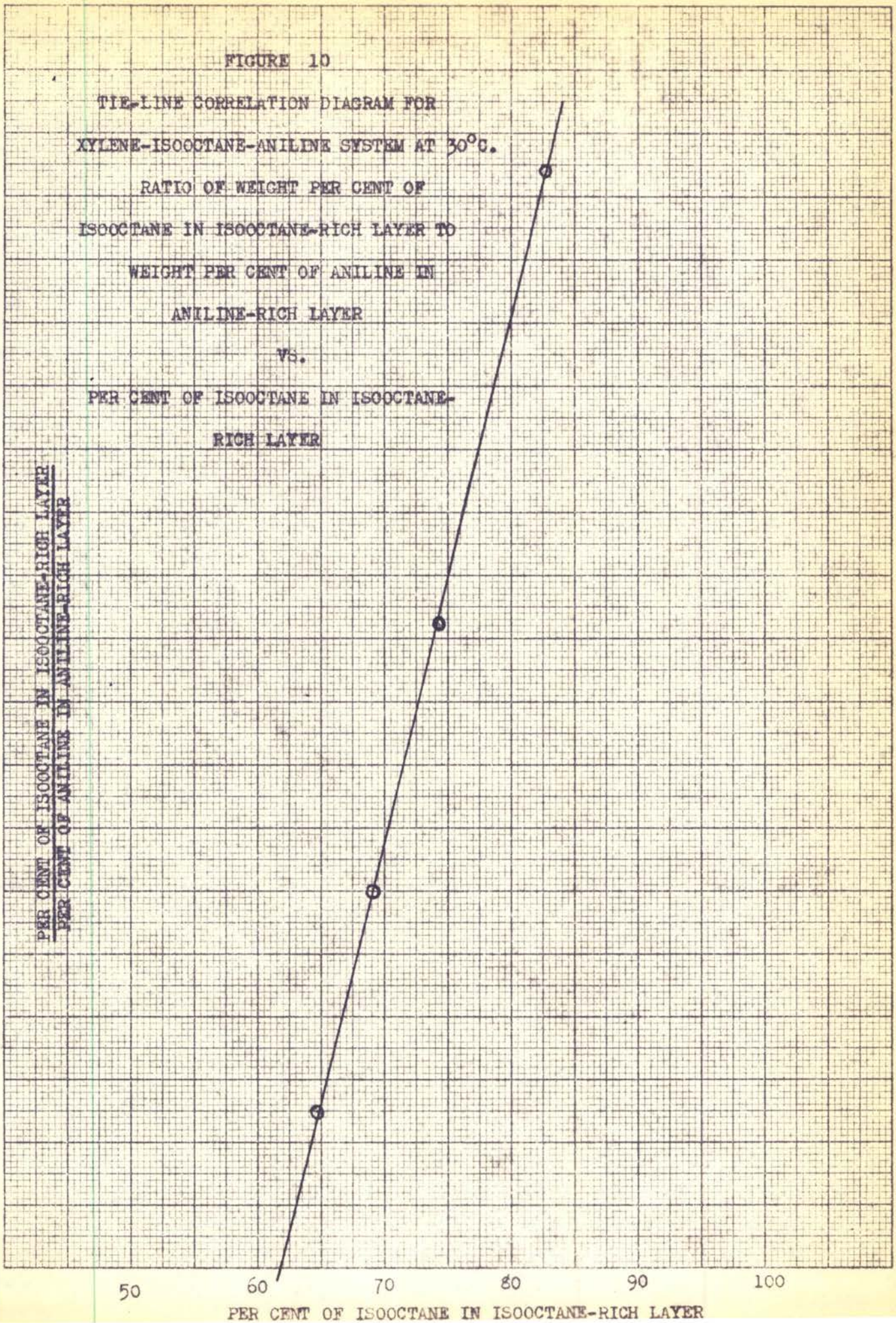


FIGURE 11

BACHMAN PLOT OF TIE-LINE DATA FOR CYCLOHEXANE-ISOOCTANE-ANILINE SYSTEM AT 20°C. IN PER CENT ISOOCTANE IN ISOOCTANE-RICH PHASE PER CENT ANILINE IN ANILINE-RICH PHASE VS. PER CENT ISOOCTANE IN ISOOCTANE-RICH PHASE

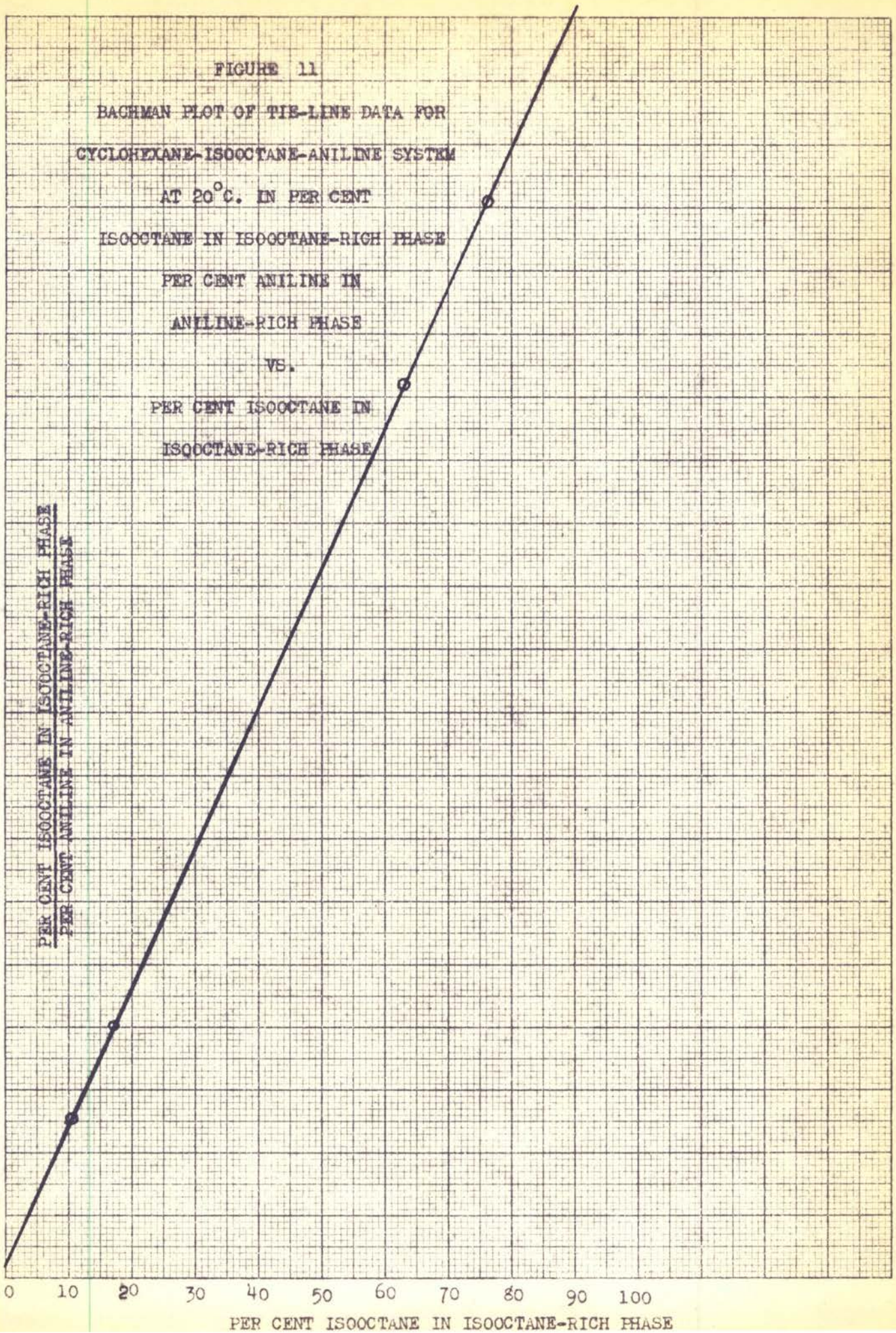


FIGURE 12

BACHMAN PLOT OF TIE-LINE DATA FOR CYCLOHEXANE-ANILINE-ISOOCTANE SYSTEM AT 30°C.

$$\frac{\text{PER CENT ISOOCTANE IN ISOOCTANE-RICH PHASE}}{\text{PER CENT ANILINE IN ANILINE-RICH PHASE}}$$

VS.

PER CENT ISOOCTANE IN ISOOCTANE-RICH PHASE

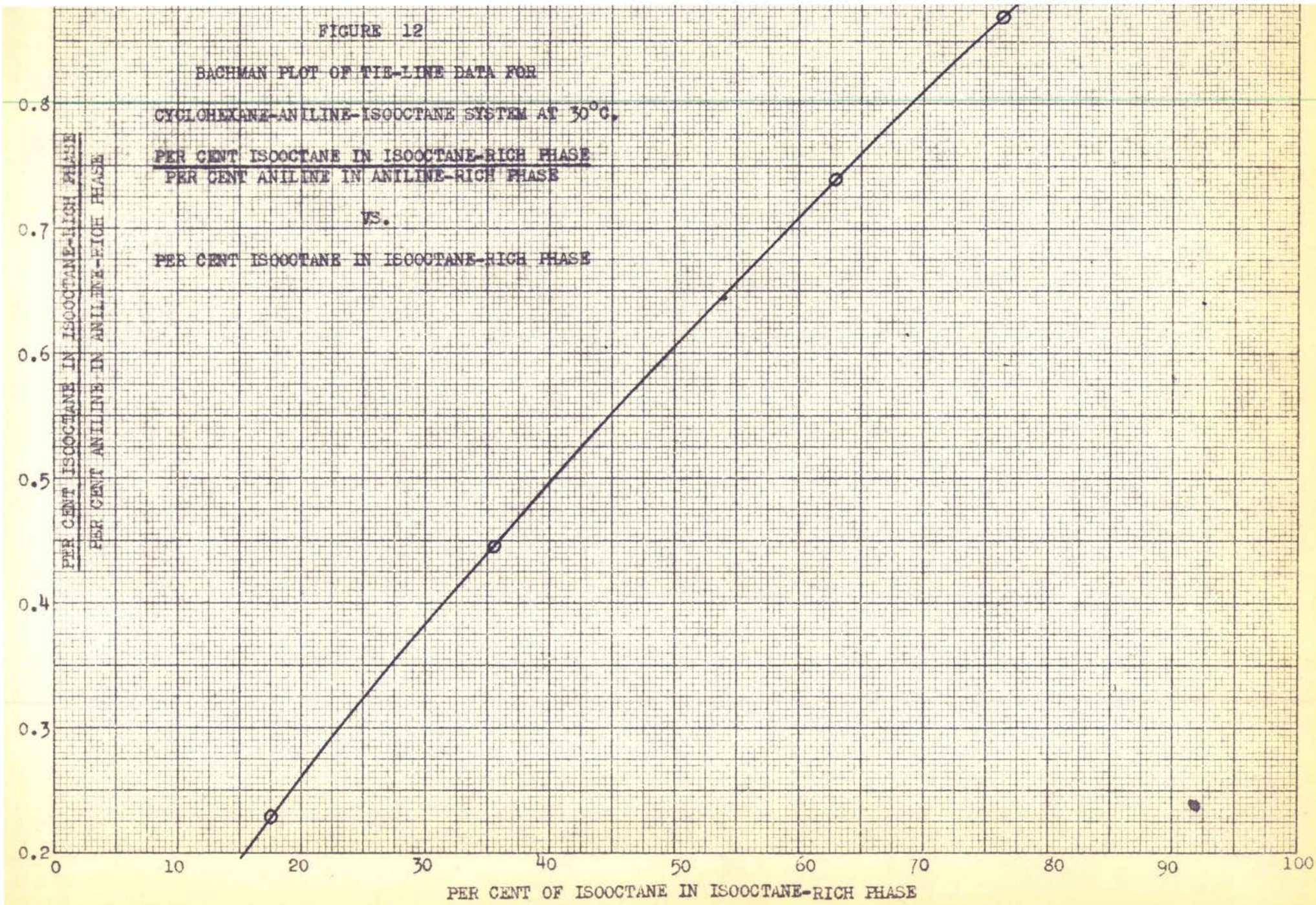


FIGURE 13

REFRACTIVE INDEX

VS.

PER CENT OF ISOOCTANE

OR

PER CENT OF ANILINE FOR THE

TERNARY SYSTEM OF CUMENE-ISOOCTANE-ANILINE

AT 20°C.

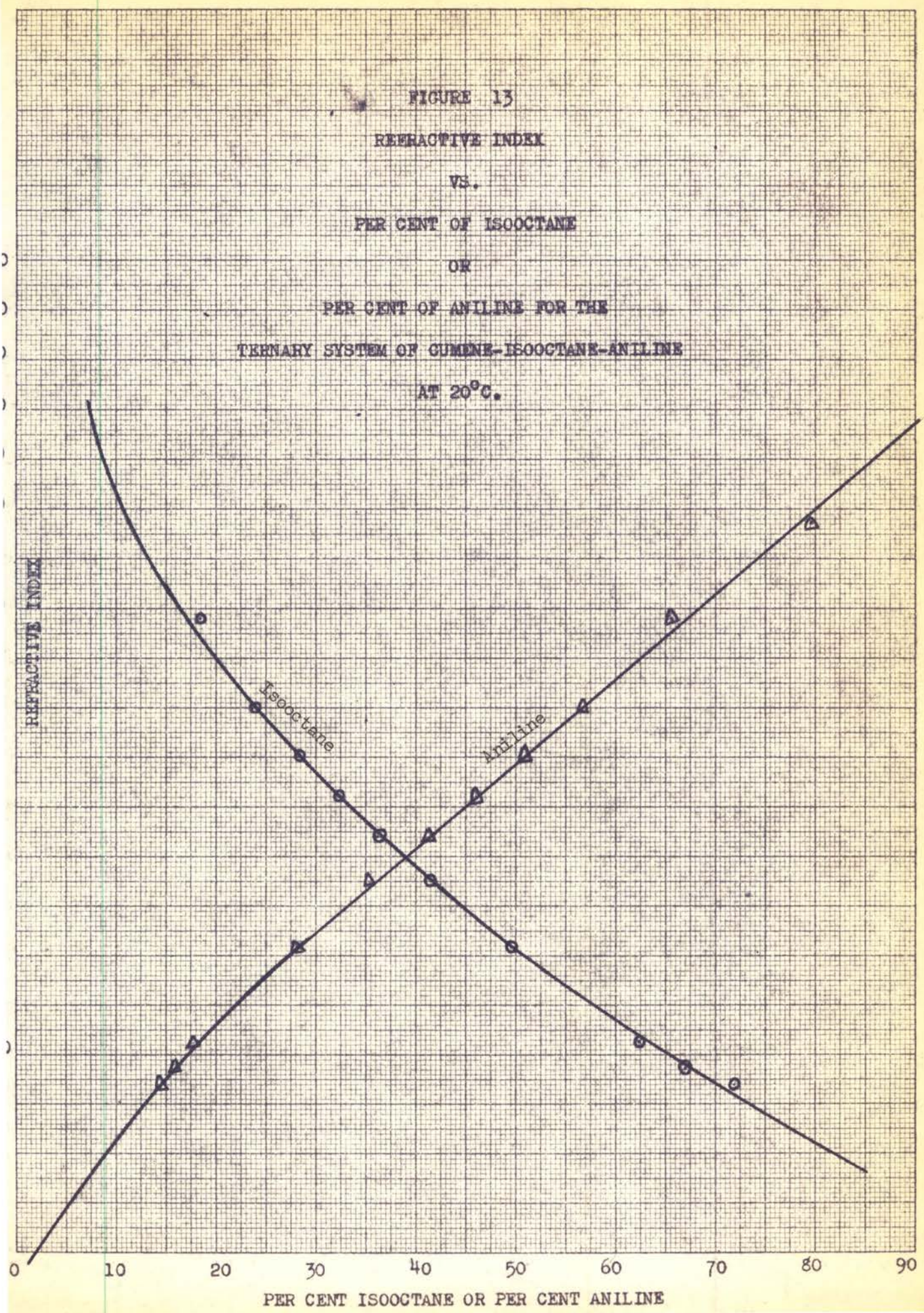


FIGURE 14

REFRACTIVE INDEX OF

CUMENE-ISOOCTANE-ANILINE SYSTEM

AT 30°C.

VS.

PER CENT OF ANILINE

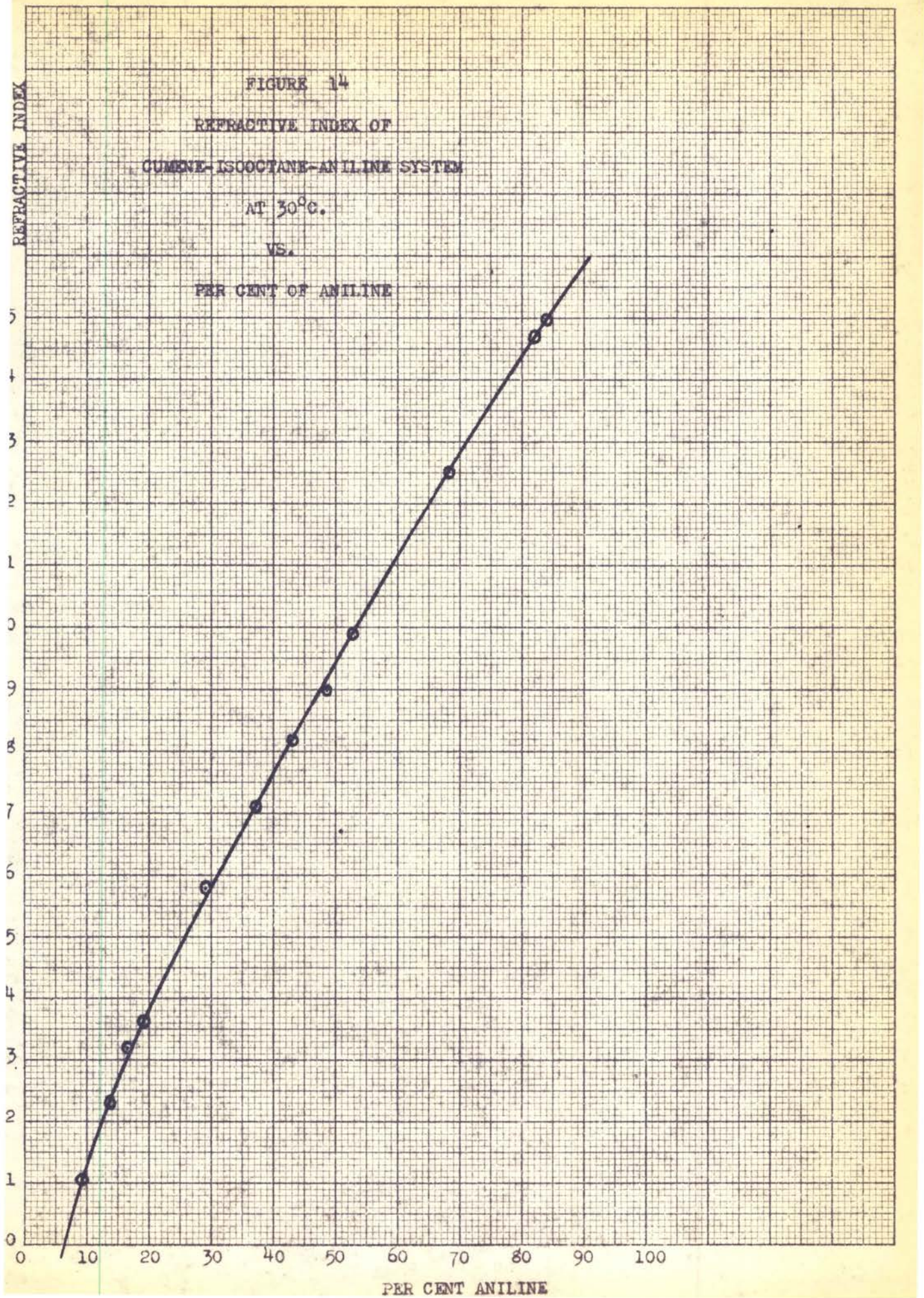


FIGURE 15

REFRACTIVE INDEX OF

CUMENE-ISOOCTANE-ANILINE

SYSTEM AT 30°C.

VS.

PER CENT ISOOCTANE

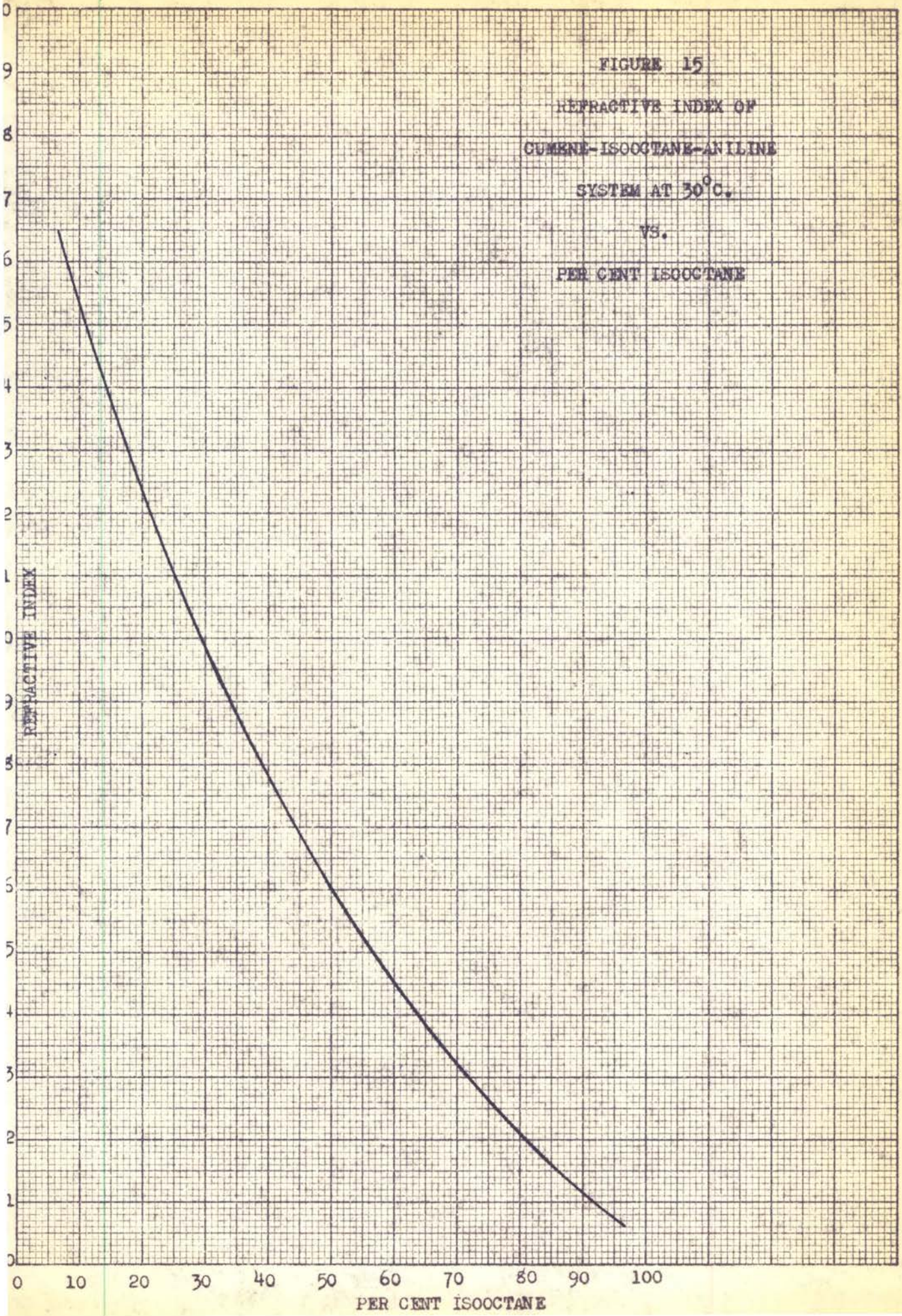


FIGURE 16

REFRACTIVE INDEX OF

XYLENE-ISOOCTANE-ANILINE SYSTEM

AT 20°C.

VS.

PER CENT OF ISOOCTANE

OR

PER CENT OF ANILINE

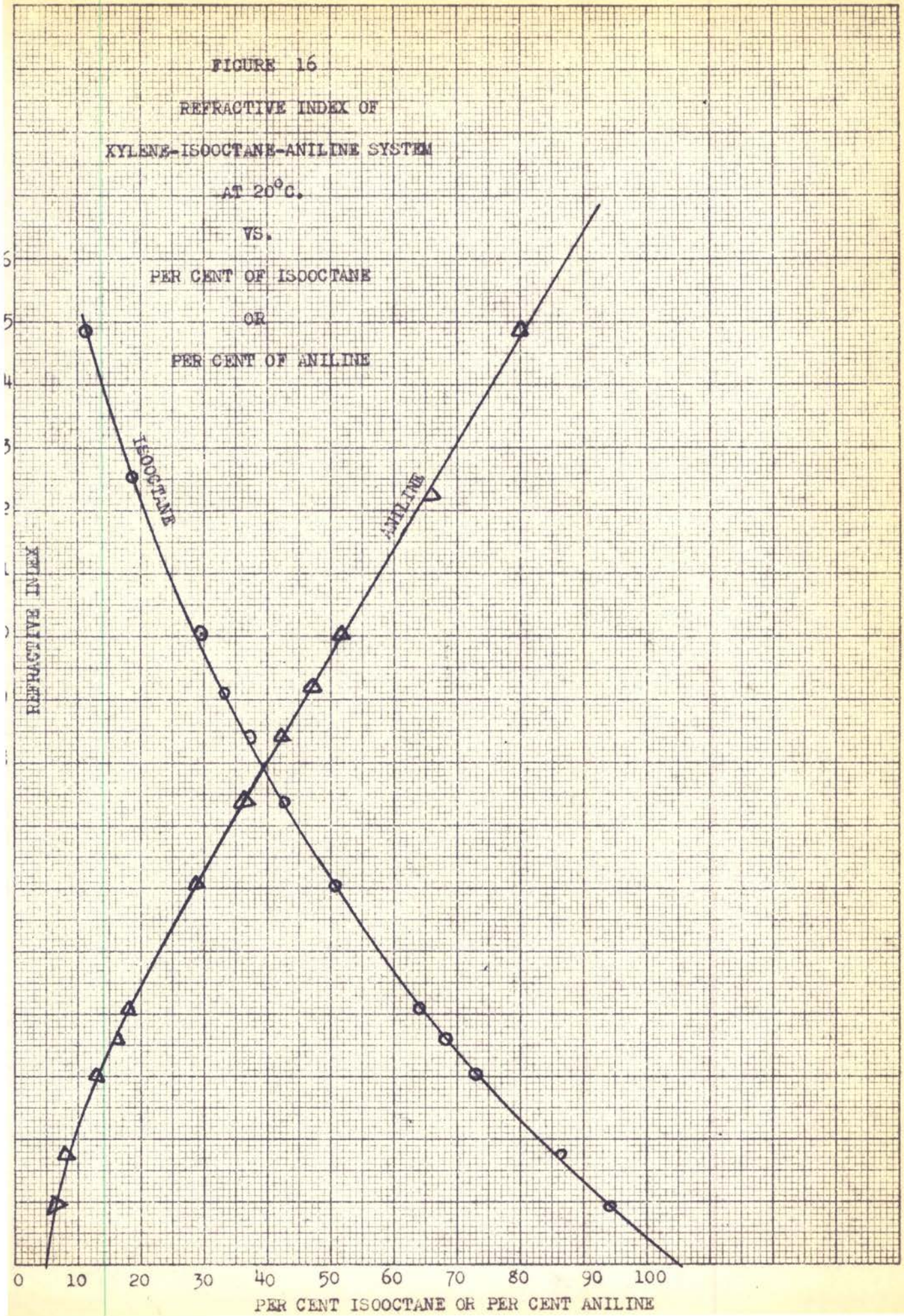


FIGURE 17

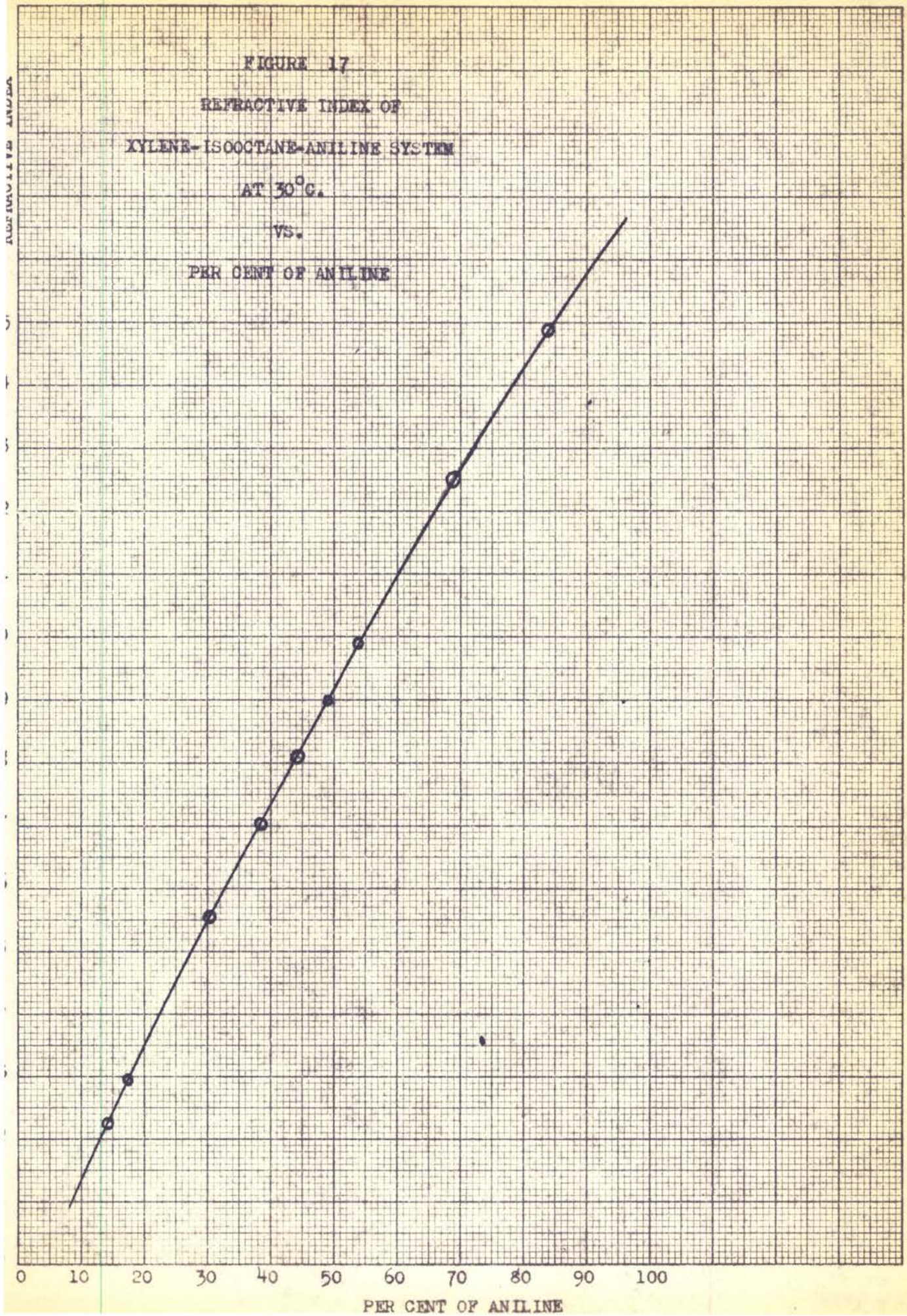
REFRACTIVE INDEX OF

XYLENE-ISOOCTANE-ANILINE SYSTEM

AT 30°C.

VS.

PER CENT OF ANILINE



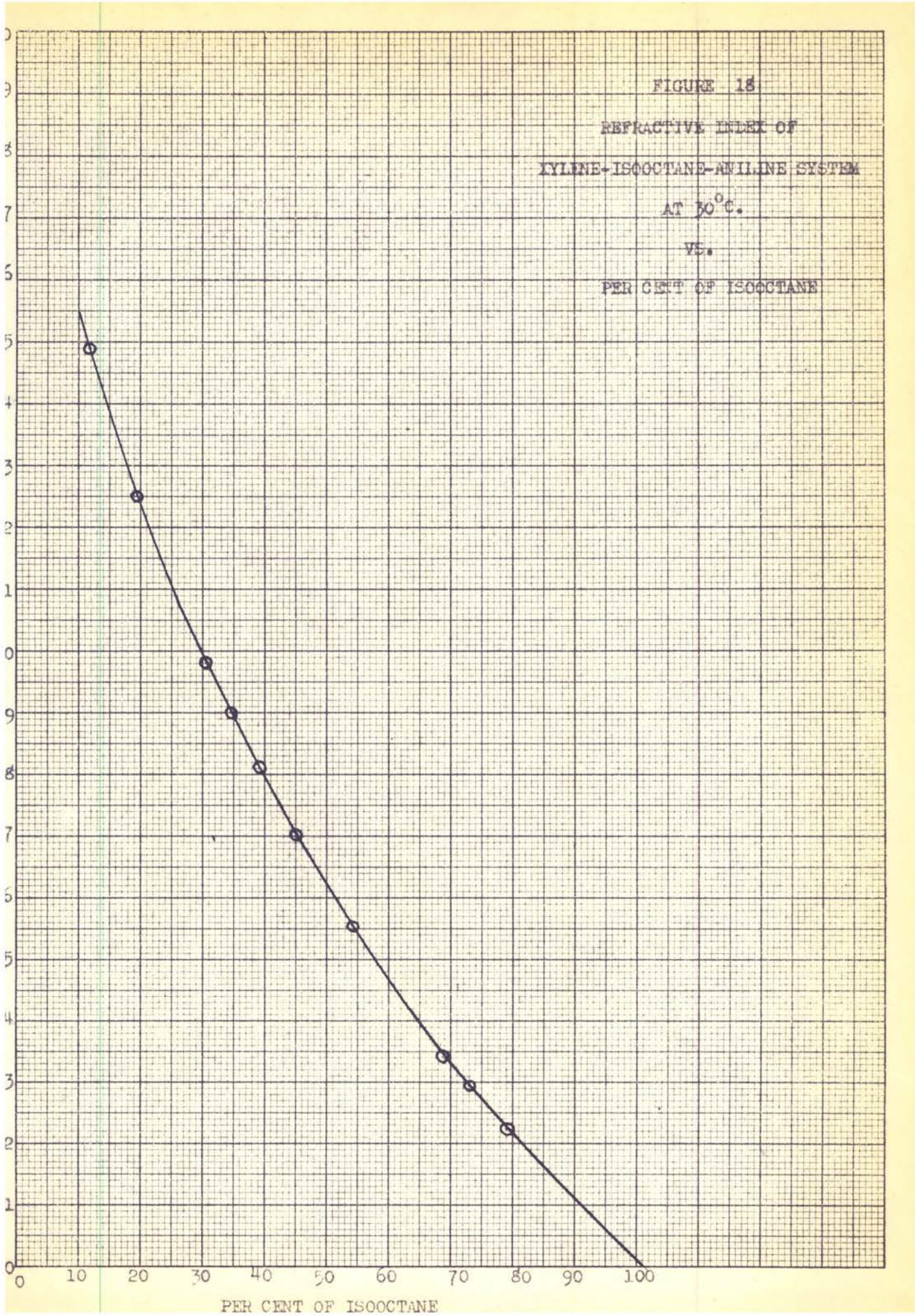


FIGURE 18
REFRACTIVE INDEX OF
XYLENE-ISOOCTANE-ANILINE SYSTEM
AT 30°C.
VS.
PER CENT OF ISOOCTANE
0
10
20
30
40
50
60
70
80
90
100
PER CENT OF ISOOCTANE

FIGURE 19

REFRACTIVE INDEX OF

CYCLOHEXANE-ISOOCTANE-ANILINE SYSTEM

AT 20°C.

VS.

PER CENT ANILINE IN ANILINE-RICH LAYER

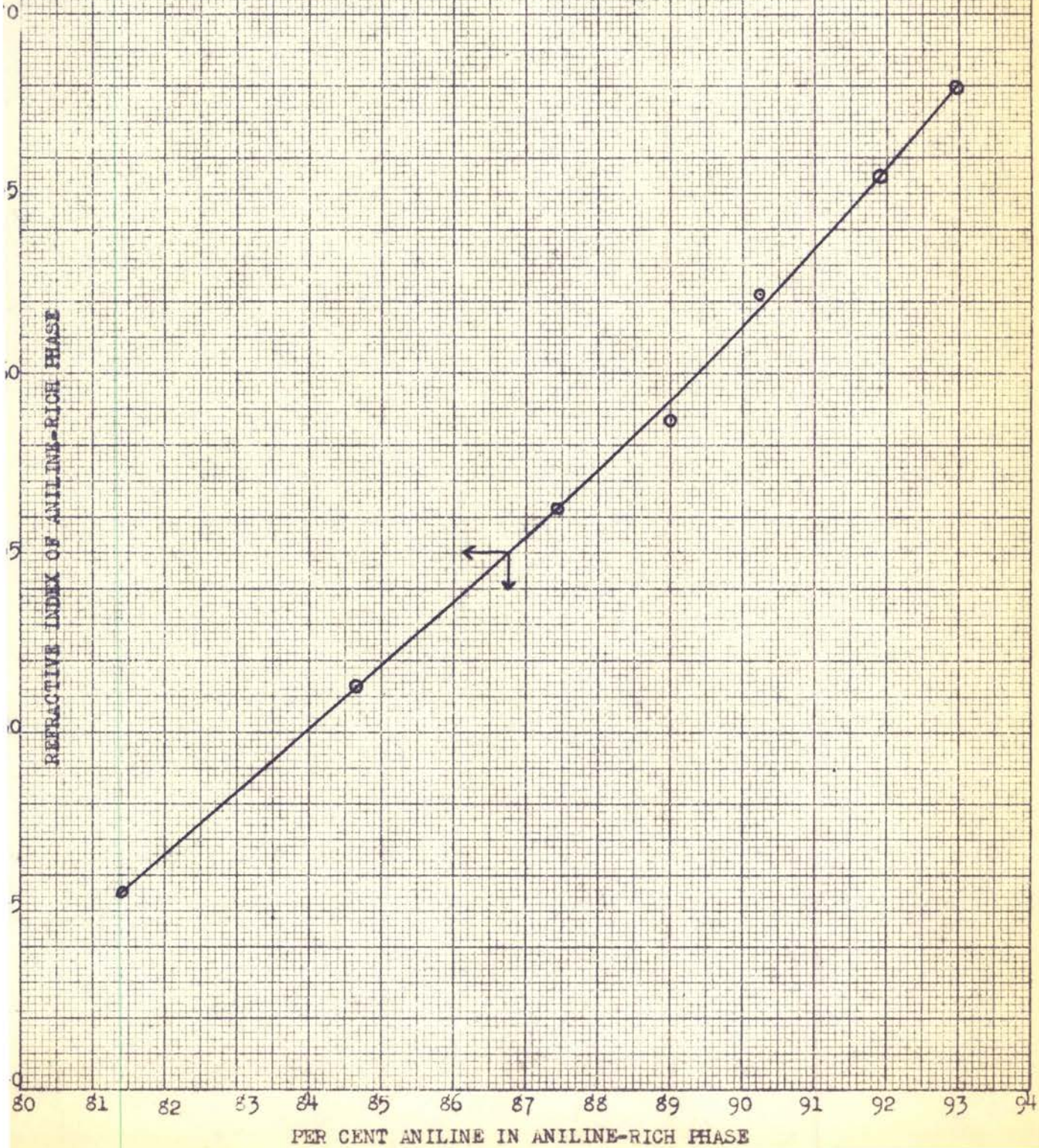


FIGURE 20

REFRACTIVE INDEX OF

CYCLOHEXANE-ISOOCTANE-ANILINE SYSTEM

AT 20°C.

VS.

PER CENT ISOOCTANE IN ISOOCTANE-RICH PHASE

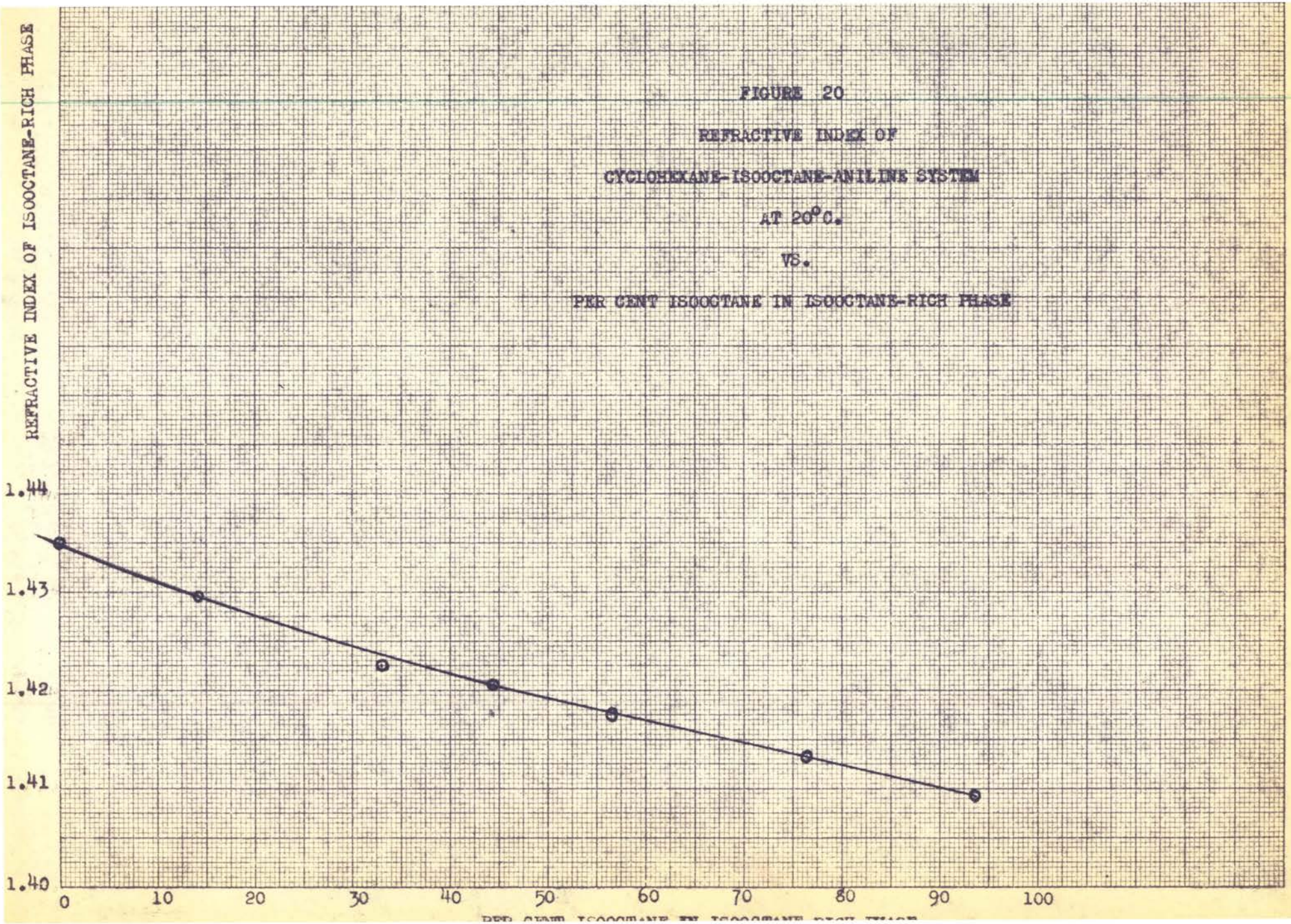


FIGURE 21

REFRACTIVE INDEX OF

CYCLOHEXANE-ANILINE-ISOOCTANE SYSTEM

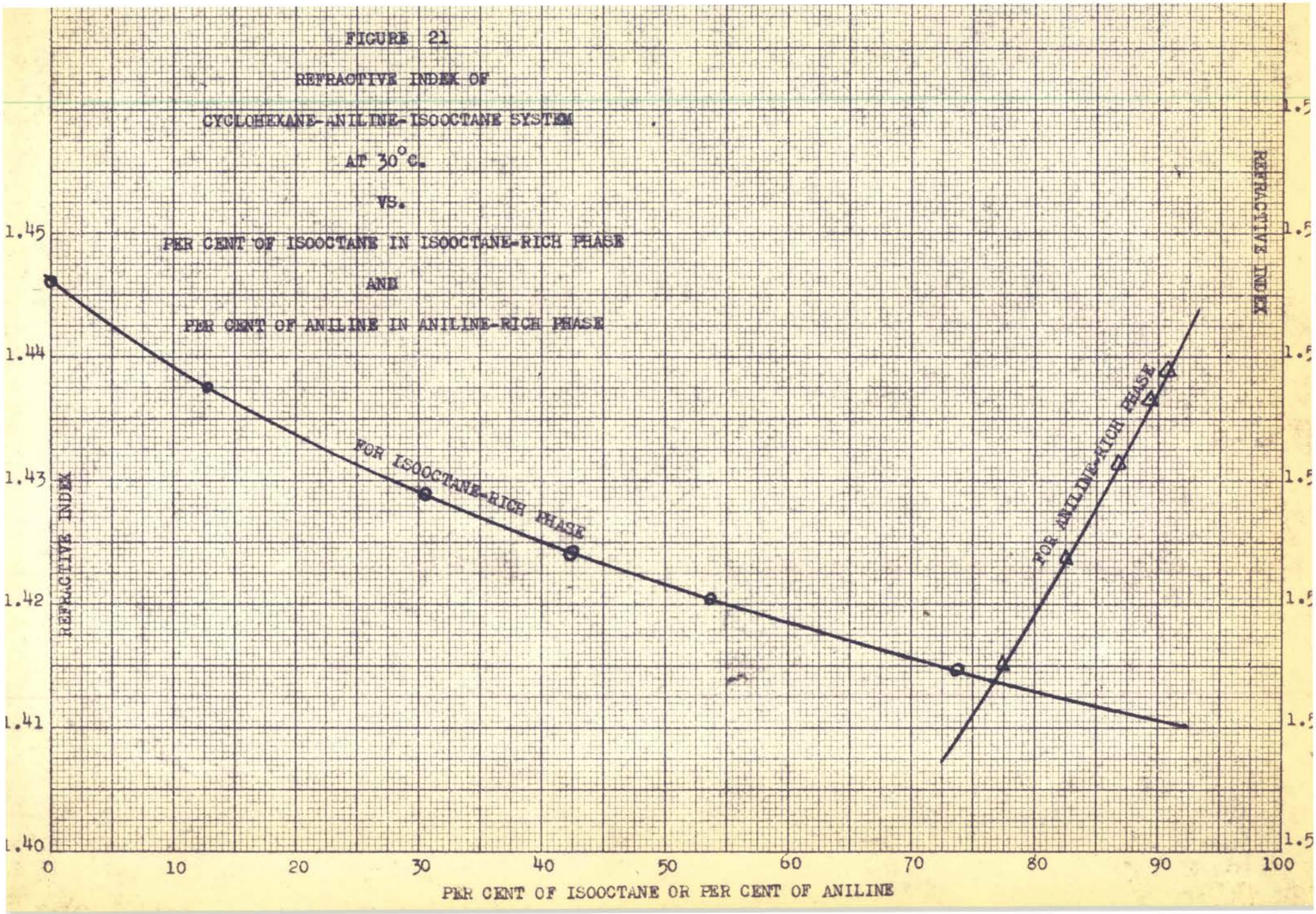
AT 30° C.

VS.

PER CENT OF ISOOCTANE IN ISOOCTANE-RICH PHASE

AND

PER CENT OF ANILINE IN ANILINE-RICH PHASE



VITA

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The content and form have been checked and approved by the author and thesis adviser. Changes or corrections in the thesis are not made by the Graduate School office or by any committee. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

TYPIST: Marianna Brown